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# SZILARD-CHALMERS REACTION IN SOME RHENIUM COMPOUNDS

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(*Received* 19 *December* 1955)

**Abstract**—This work was initiated in an attempt to contribute information on the behaviour of rhenium compounds when undergoing the Szilard-Chalmers reaction. Several compounds of rhenium were prepared, and from these experiments some preparations have been more carefully elaborated than had previously been done. An interpretation of perrhenate irradiations was made on the basis of a theory of rapid recombination of recoil fragments within a solvent molecule "cage." While an indication of dependence of retention upon degree of covalency of the ligand bonds in rhenium complex compounds was found, the dependence was not conclusively attributed to this property alone. The best method of producing high-specific-activity radioactive perrhenate solutions found in this work was by irradiation of an aqueous solution of potassium heaxchlororhenate(IV).

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## INTRODUCTION

ALTHOUGH the Szilard-Chalmers technique of production of high-specific-activity preparations of radioactive materials was first applied to iodine[1] and subsequently to other halogens,[2, 3, 4] the method was quickly extended to the thermal neutron irradiation of simple and complex inorganic compounds in order to isolate radioactive isotopes of the metallic elements.[2, 5, 6]

Various explanations of the mechanism by which the Szilard-Chalmers process functions have been offered since its first use. Some of the proposed mechanisms have been genuinely disproven as accurate representations of the process in particular systems. However, it appears that all suggested mechanisms could be applicable and valid in certain systems. Following SZILARD and CHALMERS's interpretation of actual dislodging of atoms by mechanical impact of neutrons, there arose explanations based on recoil of atoms from gamma emission,[2] recoil of atoms from conversion electrons,[7] disruption of molecules by a high state of electronic excitation following the loss of a conversion electron,[8] and bond ruptures due to high positive charges incurred by the Auger process.[9, 10] Theoretical calculations relative to the latter explanation[10, 11] were followed by experimental observations[12, 13] which were inconsistent with predictions of these calculations.

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[1] L. SZILARD and T. CHALMERS *Nature* **134,** 462 (1934).
[2] E. AMALDI, O. D'AGOSTINO, E. FERMI, B. PONTECORVO, F. RASETTI, and E. SEGRE *Proc. Roy. Soc., London* **A149,** 522–58 (1935).
[3] O. ERBACHER and K. PHILIPP *Ber.* **69B,** 893–98 (1936).
[4] O. D'AGOSTINO *Gazz. chim. ital.* **65,** 1071 (1935).
[5] F. A. PANETH and J. W. J. FAY *Nature* **135,** 820 (1935).
[6] J. IRVINE JR. *Phys. Rev.* **55,** 1105 (1939).
[7] E. SEGRE, R. S. HALFORD, and G. T. SEABORG *Phys. Rev.* **55,** 321–22 (1939).
[8] G. T. SEABORG, G. FRIEDLAENDER, and J. W. KENNEDY *J. Amer. Chem. Soc.* **62,** 1309–10 (1940).
[9] D. DEVAULT and W. F. LIBBY *Phys. Rev.* **58,** 688–92 (1940).
[10] E. P. COOPER *Phys. Rev.* **61,** 1–5 (1942).
[11] J. L. MAGEE and E. F. GURNEE *J. Chem. Phys.* **20,** 894–98 (1952).
[12] W. H. HAMILL and J. A. YOUNG *J. Chem. Phys.* **20,** 888–94 (1952).
[13] W. H. JOHNSTON *J. Chem. Phys.* **21,** 1499–1502 (1953).



1

LIBBY[14] carried out an extensive investigation on the behaviour of permanganate solutions and solid permanganates under thermal neutron bombardment. In aqueous permanganate solutions, he found that the neutron bombardment produced activity in a lower valence state, i.e. manganese(IV) oxide. The distribution of activity between the two valence states of manganese varied with the pH of the solution. Irradiation of solid potassium permanganate and subsequent solution in aqueous media of various pH values produced similar results. Interpretation of these data was based on the premise that one or two oxygens are separated from the permanganate ion by neutron capture recoil. The unstable manganese entities so formed interact with water or hydroxide ions to produce the final stable products.

HERR[15] gave a rather brief report of experiments analogous to those of LIBBY, but using compounds of rhenium. Similar irradiation conditions for perrhenates produced no activity in rhenium(IV) oxide or in any insoluble material other than the original perrhenate. Potassium hexachlororhenate(IV) and rhenium(III) chloride were found to retain activity in the original valence state only when these substances were irradiated in the solid state.

This research was undertaken to perform the irradiations of rhenium-containing compounds under more clearly defined conditions than those described in HERR'S article and to extend the work to other rhenium compounds.

## APPARATUS AND METHODS

Samples were irradiated with neutrons from a radium-beryllium source of the compressed-carbonate type. The source, containing 48·3 mg radium and providing a neutron output of 7·43 $\times$ 10 exp 5 neutrons per second, was surrounded with a cylindrical paraffin moderator. Solution samples contained in polyethylene screw-cap bottles were placed around the periphery of the moderator, thus providing one inch of paraffin between each sample and the source. Irradiations were carried out for a minimum of four days. The produced rhenium activities having half-lives significant to the tracer detection in this work were 92·8-hour rhenium-186 and 16·9-hour rhenium-188.[16]

All radioactivity measurements were made on liquid samples contained in a thin-wall jacketed counting tube. This GM tube was connected to a Nuclear Model 165 scaling unit by means of shielded cable. Counting rates were corrected for dilution and decay. A Beckman Model H2 pH meter was used for pH measurements.

The rhenium used in this work was obtained in the form of rhenium(VII) oxide from the Department of Chemistry of The University of Tennessee. Perrhenic acid solutions were prepared by dissolving the oxide in distilled water. Nitron, which was used as the precipitant for perrhenate in analytical determinations, was purchased from Fisher Scientific Company. Tetron, the precipitating agent for potassium hexachlororhenate(IV), was prepared according to directions given by Welcher.[17]

All other chemicals were reagent or C.P. grade.

[14] W. F. LIBBY *J. Amer. Chem. Soc.* **62**, 1930–43 (1940).
[15] W. HERR *Z. Naturforschung* **76**, 55–6 (1952).
[16] J. M. HOLLANDER, I. PERLMAN, and G. T. SEABORG *Rev. Mod. Physics* **25**, No. 2, 469–651 (1953).
[17] F. J. WELCHER *Organic Analytical Reagents, Vol.* 2, D. Van Nostrand Co., Inc., New York, N.Y., 1947, p. 462.

## PREPARATION OF COMPOUNDS

*Rhenium(IV) oxide.* Rhenium(IV) oxide-hydrate was prepared by the reduction of potassium perrhenate with hydrazine in a strongly basic aqueous solution, as reported by NODDACK and NODDACK.[18] The quantities of starting materials and volumes of solutions were not specified by these authors, but the following procedure was found quite satisfactory. Forty millimoles of finely ground potassium perrhenate were suspended in approximately 40 ml of hot 50% sodium hydroxide solution by rapid stirring. Ninety millimoles of finely ground hydrazine sulphate were added slowly. The reaction mixture was held at about 50° for one half hour, and the solution was then adjusted to a pH value of 4 to 6. The very finely-divided black product was collected on a fritted-glass filter and dried by vacuum desiccation over calcium chloride. The yield was almost 100%. Dehydration of the dried rhenium(IV) oxide-hydrate was carried out by heating to 350° under high vacuum for six hours.[19]

*Potassium hexachlororhenate(IV).* Preparation of potassium hexachlororhenate (IV) by proceeding through the hexachlororhenic(IV) acid intermediate has been described only briefly in the literature.[20] The following procedure yields a pure product in satisfactory yield. Ten millimoles of potassium perrhenate was reduced to rhenium(IV) oxide-hydrate by the above method. The product was washed carefully with slightly acidic water and was not dried before use in the next step. The material was digested in 15 ml of concentrated hydrochloric acid at a temperature of 85° for approximately 30 min. The dark opaque solution, green in thin layers, thus formed was passed through a fritted-glass filter. Addition of a solution of 23 millimoles of potassium chloride dissolved in 5 ml of distilled water to the hot filtrate produced a light green crystalline precipitate, which was purified further by recrystallization from 40 to 50 ml of hot concentrated hydrochloric acid. Yields in excess of 50% were easily obtained. The final product was analysed for rhenium content by oxidizing the rhenium to perrhenate with hydrogen peroxide and determining the perrhenate by nitron precipitation.

*Potassium hexabromorhenate* (IV). The preparation of potassium hexabromorhenate(IV) was analogous to the method used for preparing potassium hexachlororhenate(IV). Ten millimoles of potassium perrhenate were reduced to rhenium(IV) oxide-hydrate. This material was digested in 17 ml of 48% hydrobromic acid with rapid stirring for 30 min. The dark opaque solution, orange in thin layers, thus formed was filtered through a fritted-glass filter. Addition of a solution of 23 millimoles of potassium bromide dissolved in 5 ml of distilled water to the filtrate produced a dark red crystalline precipitate which was isolated by filtration and dried by vacuum desiccation over calcium chloride. A yield of around 40% was achieved. Although analyses of this product indicated that it was pure, the material may be recrystallized from approximately 50 ml of hot concentrated hydrobromic acid. In this case the product was orange, presumably due to a finer state of particle subdivision. In order to analyse for rhenium content by nitron precipitation, it was necessary to isolate the rhenium from bromide ions, since they interfere in the precipitation. Samples of the material were hydrolysed in strongly basic solution forming rhenium(IV) oxide and perrhenate, the perrhenate resulting from disproportionation reactions occurring

[18] I. NODDACK and W. NODDACK *Z. angew. Chem.* **44**, 215–20 (1931).
[19] E. E. AYNSLEY, R. D. PEACOCK, and P. L. ROBINSON *J. Chem. Soc.* 1622–24 (1950).
[20] I. NODDACK and W. NODDACK *Z. anorg. allgem. Chem.* **215**, 129–84 (1933).

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during the hydrolysis.[18] The perrhenate in this mixture was reduced to rhenium(IV) oxide-hydrate by the addition of a small amount of hydrazine sulphate. The combined rhenium(IV) oxide-hydrate precipitate was isolated by filtration. The carefully washed precipitate was oxidized to a perrhenate solution with hot alkaline hydrogen peroxide solution, and the perrhenate was determined by nitron precipitation.

*Potassium hexaiodorhenate(IV).* The reduction of potassium perrhenate by potassium iodide in a concentrated hydriodic acid medium was used to prepare potassium hexaiodorhenate(IV).[21] Five millimoles of finely ground potassium perrhenate were added to a rapidly stirred solution of 10 millimoles of potassium iodide dissolved in 6·5 ml of hot 57% (sp. gr. 1·7) hydriodic acid. The isolated product was dried by vacuum desiccation over calcium chloride, and a yield of about 60% of theoretical was achieved. A preparation of potassium hexaiodorhenate(IV), by the digestion of rhenium(IV) oxide in concentrated hydriodic acid to form the hexaiodorhenate(IV) ion, was also attempted. A solution of potassium iodide was added to the resulting solution, producing a crystalline black product. Since rhenium(IV) oxide-hydrate is distinctly amorphous, the crystalline nature of the solid indicated that the hexaiodorhenate(IV) ion had been produced. However, the ease of hydrolysis of the ion seemed to produce a nonhomogeneous product.

## EXPERIMENTAL

*Rhenium(IV) oxide-hydrate–perrhenate ion exchange.* The extent of the exchange of rhenium atoms between solid rhenium(IV) oxide-hydrate and soluble perrhenate ion was determined, using a tagged perrhenate solution and freshly prepared rhenium(IV) oxide-hydrate. After stirring a slurry of the oxide in the perrhenate solution, the oxide was removed by filtration. In this case, as in all subsequent cases, the amount of activity associated with the solid rhenium(IV) oxide-hydrate was determined by counting the solution formed by dissolving the solid with hot alkaline hydrogen peroxide. Less than 5% of the original activity of the perrhenate solution was found in the rhenium(IV) oxide-hydrate.

*Perrhenate ion.* Aqueous sodium perrhenate solutions were irradiated, and these solutions were then analysed for the presence of rhenium(IV) oxide. After irradiation, the solutions were passed through freshly prepared pads of rhenium(IV) oxide-hydrate in order to remove any rhenium(IV) oxide formed during irradiation. The filtrate was considered to contain the rhenium(VII) fraction. The possibility of influence of acidity upon this system was investigated at various pH values. In two experiments, the influence of reducing agents was evaluated by the presence of sodium sulphite and potassium iodide during the irradiation. To determine the possibility of adsorption of radioactive species, a sample was stirred with charcoal during the irradiation.

A system containing perrhenate in a nonaqueous, nonoxygenated medium was provided by dissolving nitron perrhenate in pyridine. The pyridine was dried with sodium, and the sample container was carefully sealed during the irradiation.

Sodium perrhenate was irradiated and subsequently dissolved in water before analysis.

*Rhenium(IV) oxide-hydrate.* Rhenium(IV) oxide-hydrate was irradiated in the solid state and also while suspended in various solvents. The analysis for the rhenium(IV) and rhenium(VII) fractions was carried out in the manner outlined above. The solid-state sample was washed carefully with slightly acidic water, and this wash solution was considered to contain the rhenium(VII) fraction. Solid samples suspended in nonaqueous media were washed with fresh solvent and with acidified water. A semiquantitative determination of perrhenate was made by a colour-comparison spot-test method using the highly coloured thiocyanate complex of a reduced oxidation state of rhenium.[22] It was found that macro amounts of perrhenate were present at the time the samples were analysed.

*Rhenium(IV) oxide.* Samples of rhenium(IV) oxide were subjected to the same treatment given to the rhenium(IV) oxide-hydrate samples. As in the case of the hydrated oxide, rather large quantities of

[21] H. V. A. BRISCOE, P. L. ROBINSON, and A. J. RUDGE *J. Chem. Soc.* 3218–20 (1931).
[22] W. GEILMANN, F. W. WRIGGS, and F. WEIBKE *Z. anorg. allgem. Chem.* **208**, 217–24 (1932).

perrhenate were found in the solvents and wash solutions. Usually about 0·05 millimole of perrhenate was present when a sample of one millimole of rhenium(IV) oxide was irradiated.

Two differences in behaviour between rhenium(IV) oxide and rhenium(IV) oxide-hydrate were encountered in these experiments. While the hydrate oxide was found to be capable of greatly altering the pH of an unbuffered aqueous solution, rhenium(IV) oxide did not show this property. In addition, it was found that rhenium(IV) oxide was attacked only very slowly by cold aqua regia, and hot alkaline hydrogen peroxide produced no apparent solution of this compound. Digestion in dilute nitric acid was necessary to produce complete solution of rhenium(IV) oxide. The hydrated oxide was oxidized readily by cold hydrogen peroxide.

*Potassium hexachlororhenate(IV).* For the hexahalorhenate(IV) compounds, the following analytical scheme was devised to provide solution samples of the rhenium(IV) and rhenium(VII) fractions which contained no halogen atoms activated by thermal neutron reaction. The hexahalorhenate(IV) ions were removed from solution by precipitating with Tetron, and filtering. This precipitate was completely destroyed by hydrolysis in sodium hydroxide solutions, producing free Tetron, rhenium(IV) oxide-hydrate, and perrhenate. Addition of hydrogen peroxide to this mixture yielded soluble perrhenate and insoluble Tetron. After removal of the insoluble Tetron, the perrhenate was reduced to rhenium(IV) oxide with hydrazine sulphate, and the oxide was isolated by filtration. Conversion of the oxide to perrhenate yielded a halide ion-free rhenium(IV) fraction. The filtrate from the first Tetron precipitation could not be used to measure the activity associated with rhenium(VII) in these experiments in which a halide acid medium had been used in the irradiation. Therefore, the perrhenate in this fraction was reduced with hydrazine sulphate to rhenium(IV) oxide, which was removed by filtration and oxidized back to perrhenate with hydrogen peroxide. This solution then contained the radioactivity associated with the rhenium(VII) fraction.

One millimole of solid potassium hexachlororhenate(IV) was irradiated and then dissolved in 15 ml of 1 : 9 dilute hydrochloric acid, and approximately 0·1 millimole of perrhenate was added as carrier. The analytical separation scheme outlined above was applied to this solution.

TABLE 1.—RETENTION IN IRRADIATED RHENIUM COMPOUNDS

| Irradiated substances | Conditions | Per cent retention |
|---|---|---|
| Sodium perrhenate | 0·90 M solution, pH 1·9, 7·6, and 11·3 | 100 |
| Sodium perrhenate | 0·50 M solution, stirred with Norit-A charcoal during irradiation | 100 |
| Sodium perrhenate | 0·50 M solution, pH 2, 0·5 M $Na_2SO_3$ and 0·5 M NaI | 100 |
| Sodium perrhenate | Solid irradiated, then dissolved in $H_2O$ | 100 |
| Nitron perrhenate | 0·29 M solution, pyridine solvent | 100 |
| Rhenium(IV) oxide-hydrate | Solid irradiated | 38 ± 5 |
| Rhenium(IV) oxide-hydrate | In water, basic | 14 ± 5 |
| Rhenium(IV) oxide-hydrate | In aqueous perrhenate solution | 12 ± 5 |
| Rhenium(IV) oxide-hydrate | In methanol | 48 ± 5 |
| Rhenium(IV) oxide-hydrate | In *n*–propanol | 39 ± 5 |
| Rhenium(IV) oxide-hydrate | In *n*–butanol | 34 ± 5 |
| Rhenium(IV) oxide-hydrate | In toluene | 48 ± 5 |
| Rhenium(IV) oxide | Dry solid | 74 ± 5 |
| Rhenium(IV) oxide | In water | 70 ± 5 |
| Rhenium(IV) oxide | In methanol | 66 ± 5 |
| Rhenium(IV) oxide | In *n*–propanol | 70 ± 5 |
| Rhenium(IV) oxide | In *n*–butanol | 72 ± 5 |
| Rhenium(IV) oxide | In toluene | 67 ± 5 |
| Potassium hexachlororhenate(IV) | Dry solid | 70 ± 3 |
| Potassium hexabromorhenate(IV) | Dry solid | 81 ± 2 |
| Potassium hexaiodorhenate(IV) | Dry solid | 87 ± 5 |
| Potassium hexachlororhenate(IV) | 0·067 M solution, 1 : 9 dilute HCl | 0 |



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The influence of heating upon the retention was observed by placing an irradiated sample in a 110° oven for one hour, in one trial, and in a 150° oven for three hours, in another trial, before separating the rhenium(IV) and rhenium(VII) fractions. Both of these experiments indicated the same degree of change in retention, i.e. the rhenium(VII) fraction was reduced by 30–40% of the amount observed in the unheated samples.

Solutions of potassium hexachlororhenate(IV) were prepared for irradiation by dissolving one millimole of the substance in 15 ml of 1 : 9 dilute hydrochloric acid.

*Potassium hexabromorhenate(IV)*. Samples of the solid were irradiated and treated in the same manner as the potassium hexachlororhenate(IV) samples. Although Tetron has been reported previously as a precipitant for only hexachlororhenic(IV) acid of the hexahalorhenic(IV) acid series, it was found that Tetron could also be used as a precipitant for hexabromorhenic(IV) acid with sufficient completeness for these experiments. Less than 2% of the acid remained in the filtrate after treatment of 0·10 M solutions using the same procedure applied to hexachlororhenic(IV) acid outlined above. This precipitate is bright yellow in colour.

*Potassium hexaiodorhenate(IV)*. Samples of the solid were treated as above. The precipitation of hexaiodorhenic(IV) acid with Tetron was not found to be quantitative. Addition of a base to the filtrate from the Tetron precipitation caused hydrolysis of the remaining acid, producing insoluble rhenium(IV) oxide-hydrate. Therefore, the procedure previously outlined was followed with one added step. The rhenium(IV) oxide which separated from solution when the filtrate from Tetron precipitation was made basic was isolated by filtration and combined with the rhenium(IV) fraction. A visual estimate of the amount of oxide produced and also the intensity of the colour of the filtrate indicated that less than 10% of the hexaiodorhenic(IV) acid was not precipitated. If one assumes 5% disproportionation in the hydrolysis, less than 5% of the rhenium(IV) in the original irradiated sample would be included in the rhenium(VII) fraction. The Tetron precipitate of potassium hexaiodorhenate(IV) is a black crystalline material.

*Summary*. Table 1 is a survey of the results of the retention studies performed in this work. The percentage retentions refer to retention in the oxidation state of the rhenium in the original irradiated material. The error in retention for all substances except the potassium hexahalorhenate(IV) compounds is an estimate based upon consideration of the statistical error in the radioactivity measurements and of the accuracy expected in the analytical separations. The error in retention for the potassium hexahalorhenate(IV) compounds is a calculated value, i.e. the standard deviation of the mean of the results of individual runs.

## DISCUSSION

The lack of exchange of rhenium atoms between rhenium(IV) oxide-hydrate and perrhenate ion was not unexpected. The analogous system of manganese(IV) oxide and permanganate also fails to undergo exchange.[14] Heterogeneous exchange reactions occur to a considerable degree between many elements in the free state and their ions in aqueous solution. However, heterogeneous exchange between atoms of different oxidation states, neither of which are zero, usually does not occur to any extent. This is illustrated by the arsenic(III) sulphide-thioarsentate ion system and the cobalt(III) hydroxide-cobalt(II) ion system, as well as others.[23] In connection with exchange of rhenium atoms between compounds of rhenium, it should be noted that the results of the irradiation of solutions of potassium hexachlororhenate(IV) indicate that exchange between perrhenate ion and hexahalorhenate(IV) ions does not occur. Any exchange would have produced some activity in the rhenium(IV) fraction.

If one interprets the results of these experiments on the irradiation of the perrhenate ion, using the theory of LIBBY as applied to the analogous permanganate studies, one must assume a high stability of the perrhenate ion. Such an assumption seems compatible with the results from other irradiations in this work and from

[14] A. C. WAHL and N. A. BONNER *Radioactivity Applied to Chemistry*, John Wiley and Sons, Inc., New York, N.Y., 1951, pp. 351–64.

thermodynamic considerations.[24] If the perrhenate ion undergoes the analogous initial recoil process yielding positively charged rhenium(VII) fragments, the observation that 100% retention occurs independent of pH of the solution leads to the conclusion that the "hydration" regenerating perrhenate ions occurs exclusively, and the oxygenated rhenium(VII) fragments are not reduced by water. The tendency toward reduction seems small indeed, in view of the lack of effect of sulphide ions or iodide ions upon the 100% retention in perrhenate.

The irradiation of nitron perrhenate dissolved in pyridine produced the interesting result that again there was 100% retention in rhenium(VII). The attachment of the large organic base to the perrhenic acid molecule should not affect the rhenium-oxygen bonds to an extent which would influence the fundamental nature of the recoil reaction occurring in the perrhenate ion. Therefore, the same rhenium-containing recoil fragments should be found in the pyridine solution. Also in this solution are oxygen ions stripped from perrhenate ions by the recoil process and nitron molecules. The "hydration" process postulated by LIBBY in his manganese work cannot occur in this nonaqueous medium, and so some other mechanism must be operative in returning the fragments to the perrhenate state. The only oxygens available, except a small amount which is dissolved in the pyridine by its contact with the atmosphere, are the ions of oxygen stripped from the rhenium in the recoil action. Unless a rapid recombination of these oxygen ions with the rhenium-containing recoil fragments occurs, one would expect these ions to diffuse into the bulk of the pyridine medium. Recombination by collision then seems very improbable in view of the very low concentration of the recoil fragments. Therefore, an alternative process suggested is one in which the recoil fragments remain within a "cage"[25] of solvent molecules until recombination occurs, thus reforming the perrhenate species. If this solvent molecule "cage" effect operates in the pyridine medium, one might postulate such behaviour in an aqueous medium. Such a theory would eliminate the necessity of a "hydration" step and also would explain the lack of effect of sulphite and iodide ions. The observation of 100% retention in irradiated solid sodium perrhenate would be expected as a result of rapid recombination of oxygen atoms restrained by the crystal lattice in close juxtaposition with the rhenium-containing fragment. The possibility of the recoiling entity being the perrhenate ion itself requires the assumption that the perrhenate ion is not destroyed by the recoil of the rhenium nucleus in the gamma-emission process. Momentum balance in the gamma-emission process following neutron capture yields a recoil energy for the rhenium nucleus which exceeds the order of magnitude of single-bond energies. Thus, it appears that the disruption of the perrhenate ion by the (*n*, gamma) process in the rhenium nucleus is very probable.

In the experiments with rhenium(IV) oxide-hydrate, very little change in retention was found when the solid was placed in various nonaqueous solvents. If the oxygen content of the medium had any effect upon the retention, such a change should have been observed in the series of alcohols. No trend was observed. When the hydrated oxide was suspended in aqueous solutions, the retention was markedly less than the retention in the nonaqueous media or in the dry solid. In the case of rhenium(IV) oxide, there is very little difference in the amount of retention regardless of the solvent

[24] W. M. LATIMER *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., Prentice-Hall, Inc., New York. 1952 pp. 241–44.
[25] J. FRANCK and E. RABINOWITCH *Trans. Faraday Soc.* **30**, 120–31 (1934).

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used, aqueous or nonaqueous, or even if the dry solid is irradiated. An explanation of the observed differences in behaviour of the oxide and the hydrated oxide may lie in the physical character of the solid materials. The hydrate is quite amorphous. On the other hand, rhenium(IV) oxide seems to have a much more ordered and stable lattice. This is suggested by the apparent decrease in volume of the hydrate as it is dehydrated and by the refractory character assumed by rhenium(IV) oxide. If one assumes that the recoil rhenium atoms found in solution originate from the surface of the solid, the surface area will be of considerable significance in determining the degree of retention. First, it is pointed out that the retention of rhenium(IV) oxide is in general almost twice as great as that of rhenium(IV) oxide-hydrate under similar irradiation conditions. Second, it must be recalled that in strongly basic solutions rhenium(IV) oxide-hydrate becomes colloidal. These points are considered to be in support of the interpretation that the recoil rhenium atoms on the surface of the solid all assume the perrhenate state by reaction with the surrounding medium and that all recoil atoms retained in the rhenium(IV) state are situated in the interior of the particles. Such an interpretation explains the low retention of the basic aqueous suspensions of rhenium(IV) oxide-hydrate, the difference in degree of retention between the hydrated oxide and the nonhydrated oxide, and the fact that no change in retention is observed for the suspension of rhenium(IV) oxide in basic solution, whereas such a change is observed for the hydrated oxide.

The retention demonstrated by the potassium hexahalorhenate(IV) compounds may be considered from the standpoint of the effect of the halogen atom upon the retention, if one assumes that the crystal structures and particle sizes are similar. There appears to be an increase in retention as one proceeds from the chlorine-containing compound to the iodine-containing compound, although the error in the data incurs a small overlap in the retention of potassium hexabromorhenate(IV) and potassium hexaiodorhenate(IV). The increase in retention then bears a direct relationship to the covalent character of the halogen atoms, their ionic sizes, and their polarizability. The effect of covalent character upon retention in recoil reactions has been regarded by some authors as significant[26] and by others as not a contributing factor.[27]

The results of this work appear to sustain the theory that an increase in covalent character is associated with an increase in retention. However, the slight overlap in retentions and the assumption of similar crystal structures and particle sizes preclude an absolutely conclusive answer. An interesting behaviour of this series is found in that the retention bears an indirect relationship to the stability toward hydrolysis of these compounds.

The result of the irradiation of aqueous solutions of potassium hexachlororhenate(IV) is in accord with the postulation of the high stability of the perrhenate ion. Apparently all recoil rhenium atoms are oxidized by the water to perrhenate, thus yielding a retention of zero per cent in the soluble rhenium(IV) compound. This irradiation seems to offer the best promise as a means of securing high specific activity radioactive rhenium preparations. The activity is not obtained carrier-free, but a concentration factor of 10 to 100 can be obtained.

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[26] P. SUE and G. KAYES *J. chim. Phys.* **45**, 188 (1948).
[27] B. C. HALDAR unpublished work.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 9 to 14. Pergamon Press Ltd., London

# THE FISSION OF URANIUM BY $C^{13}$ IONS

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**Abstract**—The relative yields of seventeen nuclides from the fission of natural uranium by $C^{13}$ ions of maximum energy 100 MeV have been measured by radiochemical methods. The typical features of high-energy fission were observed: symmetric fission predominates; nuclides near to $\beta$ stability have significant independent yields; approximately eleven nucleons are emitted.

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## INTRODUCTION

A REVIEW of the properties of high-energy heavy ions, including the nuclear reactions which they induce, has been published by WALKER.[1] One of the most interesting features of these reactions is their use to produce elements of very high atomic number. Thus GHIORSO *et al.*[2] prepared einsteinium (believed to be $E^{246}$ and $E^{247}$) by bombarding $U^{238}$ with $N^{14}$ ions, whilst ATTERLING *et al.*[3] have described the production of fermium (believed to be $Fm^{250}$) by the reaction of $O^{16}$ with $U^{238}$. The yields of the heavy elements are very small, and GHIORSO *et al.*[2] pointed out that most of the nuclear reactions lead to fission rather than to heavy elements. HOLLANDER[4] bombarded natural uranium with $C^{12}$ ions and isolated $Ag^{112}$, $Ag^{113}$, $Sr^{91}$, and $Ba^{140}$. He decided that the cross-section for the "capture" reaction (C, $5n$)* leading to $Cf^{245}$ is smaller than the fission cross-section by a factor of at least $10^4$. MILLER[5] studied the reactions between bismuth and $C^{13}$ ions, using bismuth-loaded photographic plates, and concluded that about 50% of all nuclear reactions, excluding impact disintegration of the $C^{13}$, were fission events.

The use of heavy ions can produce compound nuclei of very high $Z$, and enables us to study the fission and other nuclear reactions of the heaviest elements at moderately high excitation energies. The probability of fission as against "capture" may be expected to increase rapidly with increasing $Z$ of the compound nucleus, and thus the production of elements of $Z > 100$ by heavy-ion bombardment is likely to be very difficult. It is also of practical interest, therefore, to study the factors which might influence the extent of fission; these being the $Z$ and $N$ of both target and projectile and the energy of the projectile.

The first requirement is to obtain a general idea of the more obvious features of heavy ion-induced fission; in particular, to show whether it has the typical features of high-energy fission. These are, briefly: predominance of symmetric fissions giving a "single humped" mass yield curve; production of nuclides near $\beta$ stability, and perhaps neutron-deficient ones, in addition to the neutron-excess nuclides typical

* Originally thought to be the (C, $6n$) reaction leading to $Cf^{244}$.

[1] D. WALKER *Progress in Nuclear Physics*, Vol. 4, Pergamon Press, London (1955).
[2] A. GHIORSO, G. B. ROSSI, B. G. HARVEY, and S. G. THOMPSON *Phys. Rev.* **93**, 257 (1954).
[3] H. ATTERLING, W. FORSLING, L. W. HOLM, L. MELANDER, and B. ASTROM *Phys. Rev.* **95**, 585 (1954).
[4] J. M. HOLLANDER UCRL-1396 (1951).
[5] J. F. MILLER UCRL-1902 (1952).

of low-energy fission; emission of a considerable number of neutrons. This paper gives the results of fission-yield measurements for natural uranium bombarded with $C^{13}$ ions.

## EXPERIMENTAL

### *Irradiations*

The $C^{13}$ ions were accelerated in the Birmingham University 60-in. cyclotron. The maximum energy is ~100 MeV, but due to the manner in which heavy ions are accelerated in cyclotrons,[1] there is a considerable energy-spread and most of the ions have less than the maximum energy. The Coulomb barrier for $U^{238}$ and $C^{13}$ is ~80 MeV. Since the cross-section for ions just above 80 MeV will be low and the number of ions actually at maximum energy is small, we may take 90 MeV as the effective energy of the ions.

The uranium was in the form of foil 0·0015 in. thick (70 mg/cm²). This foil was held so as to form a quarter cylinder of radius ~2 cm and having its axis perpendicular to the plane in which the ions moved. The foil thus presented a convex curved surface to the approaching beam. Even for the ions impinging normally to its surface this foil is sufficient either to stop the ions or to reduce their energy below that required for nuclear reaction. It is also thick enough to stop all the fission fragments except those proceeding directly backwards. In most irradiations the foil was cooled by a stream of air.

Irradiation times were from ½ to 2 hr. The ion current was variable. It was not possible to measure it properly owing to the difficulty of providing R.F. shielding for the current-measuring probe and also because the beam contains many carbon ions of low energy which contribute to the ion current but not to the reaction. Experiments were made in which the outer R.F. shield had a very thin aluminium window (ca. 1 mg/cm²) in front of the uranium foil which was held on the inner (measuring) probe. This completed the R.F. shielding and also served to absorb the unwanted low-energy ions. Unfortunately, it slowed down the high-energy ions so much that very little reaction occurred, and it was found necessary to let the ions impinge directly upon the uranium.

$C^{13}$ was chosen as the bombarding particle because if $C^{12}$ were used the beam could be contaminated by any deuterons or helium ions which had been left in the cyclotron from previous experiments. These ions have almost the same mass/charge ratio as $C^{12}$ and are accelerated with it.

### *Fission-yield Determinations*

The fission yields were determined in a conventional manner, as follows. The foil was dissolved in acid together with appropriate carriers (usually 10 mg of each element) and the required elements were separated and purified. The procedure described by MEINKE[6] was used to purify the tin. The rare earths and yttrium were treated by an ion-exchange method described by CUNINGHAME[7]. The remaining elements were treated by procedures similar to those given in the National Nuclear Energy Series, Vol. 9,[8] with the following principal modifications. *Strontium*: included scavengings by $BaCl_2 \cdot H_2O$ and a precipitation of $SrCrO_4$ before the final $SrSO_4$ precipitation. *Molybdenum and cadmium*: final precipitations as 8-hydroxyquinoline complexes. *Barium*: several Fe $(OH)_3$ scavengings were included. The final precipitates were collected on small filter-paper discs, dried, and weighed to obtain chemical yields. These precipitates, mounted on aluminium trays, were counted in an internal-source $2\pi$ proportional counter. The necessary counting corrections for many fission products in this type of counter have been measured by CUNINGHAME *et al.*[9] In cases where no measurements were available, the corrections were estimated from the available data on substances of similar $\beta$ energy and chemical form. The necessary corrections for the presence of radioactive daughters (e.g. $In^{115}$ in $Cd^{115}$, $La^{140}$ in $Ba^{140}$) were also obtained from growth and decay curves measured by CUNINGHAME *et al.*[9] Initial counting rates varied from 50 to 10,000 counts/min, according to yield and half-life, compared to a counter background of 40 counts/min.

The half-lives observed for the nuclides were in good agreement with those reported,[10] due

[6] W. W. MEINKE AECD-2738 (1949).
[7] J. G. CUNINGHAME, M. L. SIZELAND, H. H. WILLIS, J. EAKINS, and E. R. MERCER *J. Inorg. Nucl. Chem.* **1**, 163, (1955).
[8] National Nuclear Energy Series, Vol. 9. *Radiochemical Studies; The Fission products* McGraw-Hill (1951).
[9] J. G. CUNINGHAME, M. L. SIZELAND, and H. H. WILLIS A.E.R.E. C/R 1646 (1955); also unpublished work by the same authors.
[10] J. M. HOLLANDER, I. PERLMAN, and G. T. SEABORG *Rev. Mod. Phys.* **25**, 469-651 (1953).

allowance being made for poor counting statistics in some cases. However, the half-life observed for silver was always close to 5·0 h (after subtracting the 7·5-day $Ag^{111}$), whereas the accepted half-life for $Ag^{113}$ is 5·3 h. This is probably due to the presence of a small quantity of $Ag^{112}$ (3·2 h) which could be formed directly in fission and could also grow in from 21 h $Pd^{112}$ during the time between irradiation and separation of the silver (~3 h).

The irradiation time was limited to a maximum of ~2 h, and it was not possible to build up a sufficient activity of nuclides with half-lives greater than a few days. The chemistry and counting

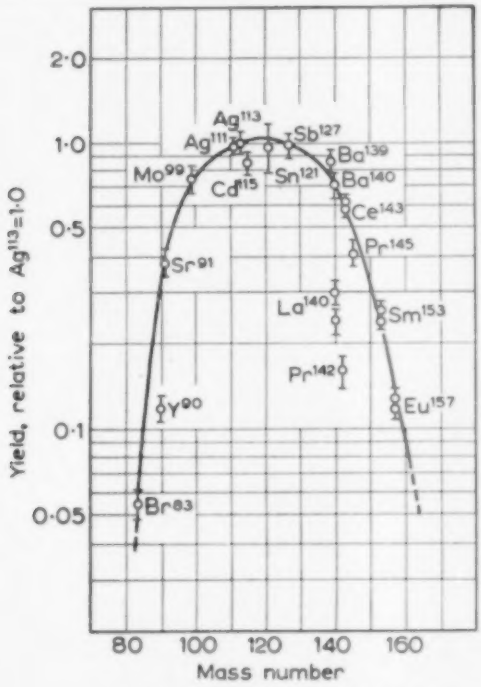


Fig. 1.—Fission of uranium by $C^{12}$ ions.

were mainly carried out at Harwell, which is eighty miles from the Birmingham cyclotron, so it was not possible to study nuclides with half-lives less than about 2 h. These considerations limited considerably the number of nuclides which could be studied, but yields were measured for seventeen nuclides in the mass-range 80–160.

The fission yields were determined only on a relative basis. $Ag^{113}$ was chosen as a reference nuclide, and a silver determination was carried out for each irradiation together with the determination of the other nuclide or nuclides. In some cases the presence of silver was not compatible with the other carrier substances (e.g. $Br^-$, or Sn in HCl solution), and a secondary reference nuclide, $Cd^{115}$ or $Mo^{99}$, was employed.

The greatest errors in these measurements are, in most cases, those associated with the counting corrections, although in a few cases the errors due to poor counting rates were comparable. An error of $\pm 10\%$ is probably reasonable for most of the relative yields, but for $Sn^{121}$, which has a low $\beta$ energy (0·38 MeV), the error could perhaps be $\pm 20\%$.

## RESULTS

The relative fission yields are shown in Fig. 1, in which the yield of $Ag^{113}$ is taken as unity. The pattern is fairly typical of high-energy fission.

Nuclides near to $\beta$ stability are formed directly in fission to a significant extent, as is shown by the yields observed for the shielded nuclides $Y^{90}$, $La^{140}$, and $Pr^{142}$. Because of this, the yields observed

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for the typical fission-product nuclides do not necessarily correspond to the total yields for the appropriate masses (as they generally do in low-energy fission-yield measurements), and the curve drawn in Fig. 1 is not, strictly speaking, a true mass-yield curve. One would not expect all the points to fall perfectly upon a curve, but rather within an envelope. The observed yields do nevertheless serve to define, rather approximately, a smooth curve (ignoring the shielded nuclides), and this curve can be used to estimate absolute yields by the usual method of normalizing the yields so that they sum to 200%. The yield for $Ag^{113}$ is then found to be 3·8%. The yields for stable nuclides and unmeasured shielded nuclides are probably significant and, since these yields are not included in the estimation, the yield of $Ag^{113}$ may well be somewhat lower than this figure.

The yield of $Cd^{115}$ (54 h) does appear to be low compared to those of neighbouring nuclides, and this is probably because some fissions lead to $Cd^{115m}$ (43 days) which is too long lived to be detected in these experiments. In thermal fission most of the mass-115 chain is formed initially as elements of lower $Z$ than cadmium, and 90% of the $Ag^{115}$ decays to $Cd^{115}$ (54 h) and only 10% to $Cd^{115m}$ (43 days). In high-energy fission some $Cd^{115}$ is probably formed directly, and the proportion of $Cd^{115m}$ (43 days) is not governed entirely by the branching ratio of $Ag^{115}$. Other workers have noted high yields of $Cd^{115m}$ (43 days) in high-energy fission.[11, 12]

The curve in Fig. 1 is symmetrical around a mass of about 120 and, since the compound nucleus has a mass of 251, this corresponds to the emission of approximately eleven nucleons either before fission or from the fission fragments. The curve is not accurately defined and so the number of nucleons lost cannot be obtained exactly.

## DISCUSSION

The kinetic energy of the $C^{13}$ ions is ~90 MeV and the binding energy of $C^{13}$ to $U^{238}$ is ~25 MeV negative, giving an excitation in the compound nucleus of ~65 MeV. The mass-yield curve obtained is closely similar to those found for the 190-MeV deuteron fission of bismuth[11] and the 340-MeV α-particle fission of uranium[13] and approximates to those found for the 250- and 340-MeV proton fissions of uranium,[12] the 190-MeV deuteron fission of uranium,[12] and the fission of bismuth and thorium by 450-MeV protons.[14] These are all reactions in which the applied energy is distinctly higher than the 65-MeV excitation involved in the $C^{13}$ induced fissions. If we consider other fissions at applied energies comparable to 65 MeV, we find that for 75-MeV protons and 50-MeV deuterons on uranium,[12] asymmetric fission of mass ratio 1:1·35 is slightly more probable than symmetric fission. In the $C^{13}$-induced fission the asymmetric fissions of mass ratio 1:1·35 are slightly less probable than the symmetric ones, the ratio of probabilities being 0·8:1.

In most high-energy fission reactions a great deal of energy is wasted in the sense that many fissions actually occur in nuclei with comparatively low excitation energies. In the first place, at energies greater than about 100 MeV, a true compound nucleus is not formed and the projectile does not pass the whole of its energy to the target nucleus. This is partly because the projectile can pass through the nucleus, making only a few collisions with individual nucleons, and thus emerge with a still considerable energy, and partly because the few nucleons which are hit can themselves emerge from the nucleus with high energy. Secondly, the excited nuclei can undergo de-excitation by successive neutron emission prior to fission.

If the target is not easily fissile, e.g. bismuth, an excited nucleus is formed in which the neutron-binding energy is lower than the fission threshold. It is supposed therefore[11] that de-excitation will proceed initially by neutron emission. As this proceeds,

[11] R. H. GOECKERMANN and I. PERLMAN *Phys. Rev.* **76**, 628 (1949).
[12] H. G. HICKS and R. S. GILBERT *Phys. Rev.* **100**, 1286 (1955).
[13] P. R. O'CONNOR and G. T. SEABORG *Phys. Rev.* **74**, 1189 (1948).
[14] P. KRUGER and N. SUGARMAN *Phys. Rev.* **99**, 1459 (1955).

the nucleus becomes more neutron-deficient and the neutron-binding energy increases; at the same time, $Z^2/A$ increases and the nucleus moves further from $\beta$ stability, so that its tendency to fission increases. Eventually a point is reached where fission can compete against neutron emission. In the process as a whole, fission competes poorly against neutron emission. For 190-MeV deuterons on bismuth, fission accounts for only 10% of the reaction cross-section,[11] for 450-MeV protons on bismuth the proportion is the same; whilst for 450-MeV protons on holmium, fission accounts for only 0·1% of the reaction cross-section.[14]

In the case of a fissile target such as uranium, the neutron-binding energy is comparable with the fission threshold. The initial interaction of a high-energy proton with a few of the target nucleons will result in emission of a few high-energy nucleons. After this, with the remaining energy distributed throughout the target nucleus, it is possible that fission competes against neutron emission without prior emission of a large number of neutrons. Fission accounts for most of the reaction cross-section.[12] It has been suggested[12] that neutrons may be emitted from the excited nucleus after it has become sufficiently distorted to cross the fission barrier, but before the fission fragments separate.

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In the case of uranium bombarded with $C^{13}$ ions, the compound nucleus has $Z = 98$ and its fission threshold should be distinctly lower than its neutron-binding energy; whereby fission could predominate over neutron emission even in the initial compound nucleus. The situation for those nuclei which did emit a neutron would be essentially unchanged, and fission would compete against emission of a second neutron. Thus in successive neutron emissions there would be strong competition from fission at every stage until in the few surviving nuclei the last possible neutron emission might finally bring the excitation to a level below the fission threshold. Fission appears to account for essentially all of the reaction cross-section.[2, 4]

Thus in heavy ion-induced fission all the available energy is used in the sense that this energy, or most of it, is present in the nuclei which fission. In the first place, such a large projectile is not likely to pass through the target nucleus, nor is it likely to transfer a high energy to only a few nucleons; thus the whole energy is deposited in the compound nucleus. Secondly, a large fraction of the fissions can occur before the loss of much energy by neutron emission. The predominance of symmetric modes of fission for an excitation of 65 MeV strongly suggests that fission does in fact occur before appreciable neutron emission. Since each neutron emitted would reduce the excitation by ~10 MeV, the loss of neutrons prior to fission would quickly reduce the excitation, so that asymmetric fission predominated.

The assumption has been made so far that a compound nucleus, $Cf^{251}$, is formed by union of target and projectile. There is evidence[5, 15] that, in the case of heavy ions and light-target nuclei at least, the target and projectile do not always fuse together entirely, i.e. only a portion of the projectile nucleus (usually one or two $\alpha$-particles) enters the target nucleus. This effect is probably of little importance for heavy-target nuclei. The fact that symmetric fission predominates seems to indicate that, in the majority of events, the whole of the available energy is used, and this implies that all the projectile enters the target nucleus. If there were, for example, a stripping reaction in which only an $\alpha$-particle was deposited in the target nucleus,

[15] K. F. Chackett and J. H. Fremlin *Phil. Mag.* **45**, 735 (1954); K. F. Chackett, J. H. Fremlin, and D. Walker *Proc. Phys. Soc. Lond.*, **A66**, 495 (1953).

it would, presumably, carry in only a fraction of the available energy and would induce predominately asymmetric fission. In the fission of thorium by 37·5-MeV α-particles, asymmetric fission is twice as probable as symmetric.[16]

It is probable that α-particles are produced in the target by impact disintegration of the carbon ions.[5] Neutrons and γ-rays may also originate in the target and to some extent extraneously on the target holder and vacuum tank walls which are also struck by energetic particles. By the same argument as that used in the preceding paragraph, one can say that if a majority of the fissions are caused by these secondary particles, then these particles must have high energies. It is unlikely that a curve such as Fig. 1 would result from fission induced in uranium by neutrons, γ-rays, protons, or α-particles of less than 50 MeV.

Although it seemed improbable that secondary particles of such energy could be present, an experiment was carried out to check the possibility. A "sandwich" foil was made, consisting of a uranium foil (70 mg/cm²), an aluminium foil (18 mg/cm²), and a second, identical, uranium foil all in close contact. This assembly was irradiated with $C^{13}$ ions normal to its surface. It was not possible to use maximum ion current, since the assembly was not cooled. The fission-product silver was isolated from each uranium foil and, whereas the front foil contained $Ag^{113}$ to the extent of 600 counts/min (measured 6 h after irradiation), the back foil contained no detectable silver activity (measured at the same time). Neutrons and γ-rays would have passed through both foils. The same is true of protons and α-particles of 50 MeV or more. The ranges in uranium of these particles at 50 MeV are, respectively, 5 g/cm² and 0·5 g/cm².

It is unlikely that the mass-yield curves for fission of other heavy elements by heavy ions will differ appreciably from that found for uranium and $C^{13}$, except for slight displacements of the peak to higher or lower masses. The yields (Fig. 1) drop by less than 10% for a displacement of 10 mass units either way from the peak. Therefore, the fission yields for the nuclides near the peak should be nearly the same in all heavy ion-induced fissions of heavy elements and the yield of silver or cadmium could be used as a convenient monitor for the number of fissions occurring in different systems.

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[16] A. S. Newton, *Phys. Rev.* **75**, 209 (1949).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 15 to 23. Pergamon Press Ltd., London

# THE COHESIVE ENERGIES OF TRANSITION METALS.

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**Abstract**—An approximate theory of the cohesive energies of first transition-series metals is presented. It is suggested that crystal field splitting is of no appreciable importance in determining these energies. Then the cohesive energy is regarded as made up of just two parts, one arising from the breakdown of intra-atomic spin couplings and the other from the formation of interatomic ones. The former is calculated in terms of atomic spectral parameters and the latter is assumed to vary smoothly along the series with a maximum in the middle. It is shown that the theory may be extended to interpret the form of variation of cohesive energies of the remaining elements of the first long period and of the second and third also. Ferromagnetic iron is discussed from the present point of view.

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## 1. INTRODUCTION

THE experimental values[1] of the heats of formation of first transition-series metals are plotted as a function of atomic number in Fig. 1. It is the purpose of this paper to propose a possible explanation for the form of their variation.

We define $\Delta H$ as the heat of the reaction

$$M_{\text{gas}} \rightarrow M_{\text{solid}}, \tag{1}$$

where $M_{\text{gas}}$ consists of neutral gaseous metal atoms in their ground state and the solid is at the absolute zero. Actually, Fig. 1 refers to the heats of reaction at 298·16°K. This is because $\Delta H$ is not available for all the metals at 0°K. One would not expect $\Delta H$ to differ much at the two temperatures—the difference is known for seven of the twelve metals and is in no case as much as 1 kcal mole$^{-1}$. The majority of these metals are polymorphic and, with the exception of manganese, they crystallize in one or more of the face-centred cubic (f.c.c.), hexagonal close-packed (h.c.p.), or body-centred cubic (b.c.c.) structures.[2] Manganese is known to have at least three structures, all of a rather more complicated kind. From our point of view, the interesting feature of this polymorphism is the extremely small heat of transition between any two known forms of the same metal. The range of variation in Fig. 1 is 100 kcal mole$^{-1}$, but none of the heats of transition are more than 0·6 kcal mole$^{-1}$.[1] Thus, for the known polymorphic forms, Fig. 1 is independent of crystal structure to a high degree of accuracy. It does not follow from this, but yet it is a natural extension to suggest, that the main features—the two-humped form with a minimum at manganese—are in no way a consequence of variation of crystal structure along the series. We shall use this idea in the subsequent discussion.

We do not intend to attempt to make an a priori calculation of $\Delta H$, but rather to use a concept which has proved useful in obtaining an approximate partial understanding of the heats of formation of transition-metal complexes. The energy (which is

[1] Selected values of Chemical Thermodynamic Properties. Circular of the National Bureau of Standards, No. 500. Washington, D.C. (1952).
[2] A. F. WELLS *Structural Inorganic Chemistry*, chapter 24. Oxford University Press (1950).

negative, corresponding to a positive $\Delta H$) of such a complex is regarded as being made up of three parts:

$$E = p + P + \lambda\Delta, \tag{2}$$

(see GRIFFITH,[3] equation 7), where $p$ is negative and varies smoothly with atomic number—it decreases nearly linearly from $Ca^{++}$ to $Zn^{++}$. $P$ is positive and is a valence-state preparation energy, this being necessary to ensure that all the ions are in a comparable state before the complex is formed. $\lambda\Delta$ arises, for regular octahedral or

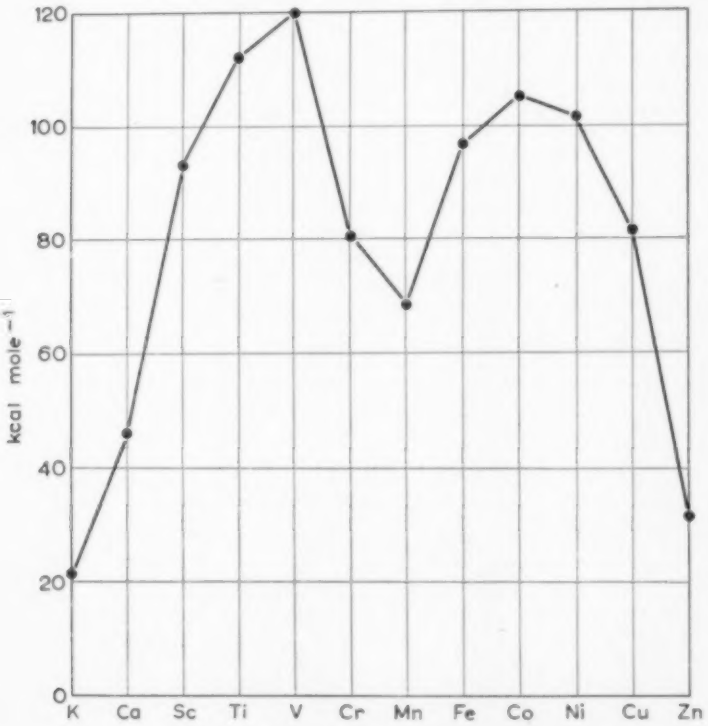


FIG. 1.—Experimental values of the cohesive energies of first transition-series metals in kilocalories per mole.

tetrahedral complexes, from the fact that the $d$ shell is split into two parts of differing orbital energy, although for metals we shall see that it is no longer of importance. $\Delta$ is this difference of energy, and $\lambda$ the number of $d$ electrons in the less stable kind of orbital. We shall use equation (2) in discussing the formation of metals from neutral atoms also, although the precise significance of the terms will be somewhat different. Before continuing, we note that the spin-orbit coupling energy is small for first transition-series elements,[4] and equation (2) was obtained by neglecting it.

Now we consider $p$. In the neutral-metal atom the $4s$ orbital is considerably below the $4p$ from potassium to zinc. From titanium to zinc, however, the $3d$ is of comparable energy with the $4s$. For this reason we suppose the total wave-function

[3] J. S. GRIFFITH *J. Inorg. Nucl. Chem.* **2**, 1 (1956).
[4] J. S. GRIFFITH *J. Inorg. Nucl. Chem.* in the press (1956).

of any of these metals to be composed mainly of configurations involving $3d$ and $4s$ atomic orbitals, but very little of configurations involving appreciable amounts of $4p$ orbitals. We have, then, six atomic orbitals on each atom available for forming bonds in the metal. This system will accommodate twelve electrons per atom in all, and we expect the binding energy $(-p)$ to increase from zero for no electrons (argon) to a maximum at or near six (chromium) and descend again to zero for twelve (zinc). Then one will have a second rise to a peak of three electrons in the $4p$ shell (arsenic), followed by a decrease to zero again for six (krypton). Actually, the assumption that all the $3d$ and $4s$ orbitals are completely used before a start is made on the $4p$ orbitals is only a rough approximation, and so we do not expect $(-p)$ to be quite zero for zinc, although we do expect it to be small. Alternatively, one could discuss the variation explicitly in terms of a simple model—perhaps an averaged-field hamiltonian molecular orbital one. Then the earlier elements have their electrons in bonding orbitals and the later in antibonding ones, giving the picture just outlined. But the form of variation to be expected for $(-p)$ rests upon more general considerations than this.

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The discussion of $p$ has assumed that all the valence electrons are used in bonding. In equation (1), $M_{\text{gas}}$ refers to the ground state of the metal atom and in it the spins of the $4s$ and $3d$ electrons are strongly coupled together. In the solid, these intra-atomic spins must be at least partially uncoupled. For convenience in calculation we make an assumption of perfect pairing (see, for example, COULSON[5]). This will be defined more carefully in the next section, but means roughly that the metal is regarded as built up of neutral atoms with the spins of any pair of electrons in different orbitals of the same atom at random with respect to each other. Now we see the significance of two of the parts of (2): $P$ is the energy required to raise the metal atom from its ground state to a nonstationary state $M_v$, in which as many electrons as possible occupy $4s$ and $3d$ orbitals singly and have their spins uncoupled; $(-p)$ is the heat of formation of the metal from this state $M_v$.

The last term of (2) is $\lambda\Delta$. For inorganic complexes, $\lambda\Delta$ was very important in determining the behaviour of $\Delta H$. However, this does not seem to be the case here. The insensitivity of $\Delta H$ to crystal structure immediately suggests that $\lambda\Delta$ is unlikely to provide an important contribution to the energy. We remember that, for inorganic complexes with octahedral symmetry around a metal atom, the $e_g$ and $t_{2g}$ $d$-orbitals could be said to differ in energy because $e_g$ pointed towards the ligands and $t_{2g}$ away. This symmetry classification still holds for atomic orbitals in the f.c.c. structure, but the reason for the energy difference is no longer there. Similarly for the h.c.p. structure, which has $D_{3h}$ symmetry around any atom, one does not expect the $d$-shell splitting, allowed on symmetry grounds, to be large. From this point of view the b.c.c. structure is not so satisfactory. However, the term $\lambda\Delta$ is only really significant when the $d$ electrons can be regarded as localized around the metal atom. The consideration of $\lambda\Delta$ for the b.c.c. case will be effectively absorbed in other considerations (see Section 5), and we shall not refer to it again. Then we take $\Delta$ to be zero, and have

$$-\Delta H = p + P. \tag{3}$$

We have already determined the form of $p$. $P$ is a purely atomic quantity, and may be

[5] C. A. COULSON *Valence* p. 166, Oxford University Press (1951).

calculated according to the usual theory of atomic spectra (with no configuration interaction).

## 2. CALCULATION OF THE VALENCE STATE PROMOTION ENERGY $P$

Unfortunately, neither $p$ nor $P$ in (3) are uniquely defined yet. This is for two reasons, the first being that we have not yet specified the electronic configuration of the valence state $M_v$. For example, for vanadium ought we to consider $3d^34s^2$, $3d^44s$, or $3d^5$? We want $p$ to vary smoothly, and so the important thing is to choose the same kind of configuration for each element. We shall take $d^{n-1}s$ for all elements (except zinc, which must be $d^{10}s^2$). This seems the most reasonable choice, but it is not essential, and I have carried through calculations for $d^{n-2}s^2$ and obtained very similar results. Then $P$ consists of two parts

$$P = P_1 + P_2, \tag{4}$$

where $P_1$ is the energy required to raise the metal atom from its ground state to the centre of gravity of the lowest term of the configuration $d^{n-1}s$. The relevant states and terms are shown in Table 1. They are all known experimentally,[6] and $P_1$ is easily obtained.

TABLE 1.—VALENCE STATE AND DERIVED THERMODYNAMIC DATA FOR FIRST TRANSITION-SERIES METALS

| Element | Ground state | Lowest term of $d^{n-1}s$ | $P_2$ | $P$ (kcal mole$^{-1}$) | $P + \Delta H$ |
|---|---|---|---|---|---|
| K | $4s$, $^2S_{1/2}$ | $4s$, $^2S$ | 0 | 0·0 | 21·5 |
| Ca | $4s^2$, $^1S_0$ | $3d4s$, $^2D$ | $\frac{1}{2}G_d$ | 59·9 | 105·9 |
| Sc | $3d4s^2$, $^2D_{3/2}$ | $3d^24s$, $^4F$ | $3B + \frac{1}{2}C + G_d$ | 44·6 | 137·6 |
| Ti | $3d^24s^2$, $^3F_2$ | $3d^24s$, $^5F$ | $5\frac{1}{2}B + 1\frac{1}{2}C + 1\frac{1}{2}G_d$ | 46·8 | 158·8 |
| V | $3d^34s^2$, $^4F_{3/2}$ | $3d^44s$, $^6D$ | $9B + 3\frac{1}{2}C + 2G_d$ | 58·5 | 178·5 |
| Cr | $3d^54s$, $^7S_3$ | $3d^54s$, $^7S$ | $14B + 6C + 2\frac{1}{2}G_d$ | 91·2 | 171·7 |
| Mn | $3d^54s^2$, $^6S_{5/2}$ | $3d^54s$, $^6D$ | $9B + 3\frac{1}{2}C + 2G_d$ | 107·4 | 175·7 |
| Fe | $3d^64s^2$, $^5D_4$ | $3d^74s$, $^5F$ | $5\frac{1}{2}B + 1\frac{1}{2}C + 1\frac{1}{2}G_d$ | 52·4 | 149·1 |
| Co | $3d^74s^2$, $^4F_{9/2}$ | $3d^84s$, $^4F$ | $3B + \frac{1}{2}C + G_d$ | 27·1 | 132·1 |
| Ni | $3d^84s^2$, $^3F_4$ | $3d^84s$, $^2D$ | $\frac{1}{2}G_d$ | 3·9 | 105·5 |
| Cu | $3d^{10}4s$, $^2S_{1/2}$ | $3d^{10}4s$, $^2S$ | 0 | 0·0 | 81·5 |
| Zn | $3d^{10}4s^2$, $^1S_0$ | ——— | ——— | 0·0 | 31·2 |

$P_2$ is the energy required to uncouple the spins. If $n \leqslant 6$, we take a determinant of one-electron functions, and the energy of the lowest term of $d^{n-1}s$ is given by

$$E = \Sigma J_{ij} - \Sigma K_{ij}, \tag{5}$$

where the sums extend over all pairs of orbitals $(i, j)$, and none of the $K_{ij}$ are zero. Then the energy of the state with random spins is

$$E_r = \Sigma J_{ij} - \tfrac{1}{2}\Sigma K_{ij}, \tag{6}$$

giving

$$P_2 = \tfrac{1}{2}\Sigma K_{ij}. \tag{7}$$

[6] C. E. MOORE *Atomic Energy Levels* Circular of the National Bureau of Standards, no 467, vols 1 and 2. Washington, D.C. (1949, 1952).

For $n > 6$ it is always possible to express the ground-state wave function as a single determinant consisting of a certain number of doubly-occupied space orbitals and other singly-occupied ones. Then $P_2$ is still given by (7), but the sum now runs only over pairs of the singly-occupied ones.

The second reason why $P$ is not uniquely determined is now apparent. For a single-determinant wave function, $E$ in (5) is invariant to an orthonormal transform of the constituent one-electron spin orbitals. But $P_2$ is not. We have already, in neglecting $\lambda\Delta$, regarded the metal as effectively uniform, and here we take our constituent orbitals as those appropriate to spherical symmetry—namely, those quantized with respect to their orbital angular momentum about an arbitrary specified axis. This is in agreement with our assumption about the independence of $\Delta H$ of crystal structure (if, instead, one uses real orbitals appropriate to a cubic field, $P_2$ is slightly reduced. However, $P$ is in every case reduced by less than 13%). $P_2$ is now uniquely defined, and its expression in terms of atomic spectral parameters $B$, $C$, and $G_d$ is shown in Table 1. $B$ and $C$ are RACAH's parameters for use with $d$ electrons[7] and $G_d$ is the exchange integral between a $3d$ and a $4s$ electron:

$$G_d = \langle 3d4s\,|V|\,4s3d\rangle, \tag{8}$$

with $V$ the electrostatic energy. Values of $B$, $C$, and $G_d$ obtained by CATALAN, ROHRLICH, and SHENSTONE[8] in an analysis of the empirical data were used to obtain numerical values for $P_2$. The resulting values of $P$ are shown in column 5 of Table 1, and $\Delta H + P$ in the last column.

According to equation (3), this last quantity is $(-p)$. It is plotted in Fig. 2 against atomic number. We see that it is very close to the expected form and that the dip in the middle of Fig. 1 has been almost entirely removed.

## 3. THE ELEMENTS OF THE SECOND AND THIRD LONG PERIODS

The theory just developed can also be used to discuss, in a general way, the heats of formation of the remaining elements of the first long period and all the elements of the second and third. We shall not do this in detail, but make a few general observations. In the first place, in the second and third long periods the electrostatic integrals are smaller, so the dip in the centre of the transition series should be less marked. Then we must consider the spin-orbit coupling energies, especially for the third series. These were discussed by the author[4] for metal complexes, and very similar conclusions apply here—namely, that their effect upon the form of the plot of $\Delta H$ is in the opposite direction from that of $P$. For this reason also, particularly in the third series, the dip in the centre should be reduced. These observations are borne out in practice. The experimental values of $\Delta H$[1, 9] for all three periods are plotted as a function of atomic number in Fig. 3. The fourteen rare-earth elements, cerium to lutetium inclusively, have been omitted, partly for lack of data but also to bring out the correspondences between the three periods. We see that there is a marked dip at technetium, but not nearly so large as at manganese; in the third period there seems to be no dip at rhenium.

[8] G. RACAH *Phys. Rev.* **62**, 452 (1942).
[7] M. A. CATALAN, F. ROHRLICH, and A. G. SHENSTONE *Proc. Roy. Soc.* **A221**, 421 (1954).
[9] L. BREWER *Chemistry and metallurgy of miscellaneous materials: Thermodynamics* paper 3, p. 13. McGraw Hill (1950).

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If we accept the theory presented in this paper, then Fig. 3 shows that we can understand in simple general terms the form of variation of cohesive energy from argon to radon (in fact, right through the periodic table, from hydrogen at least as far

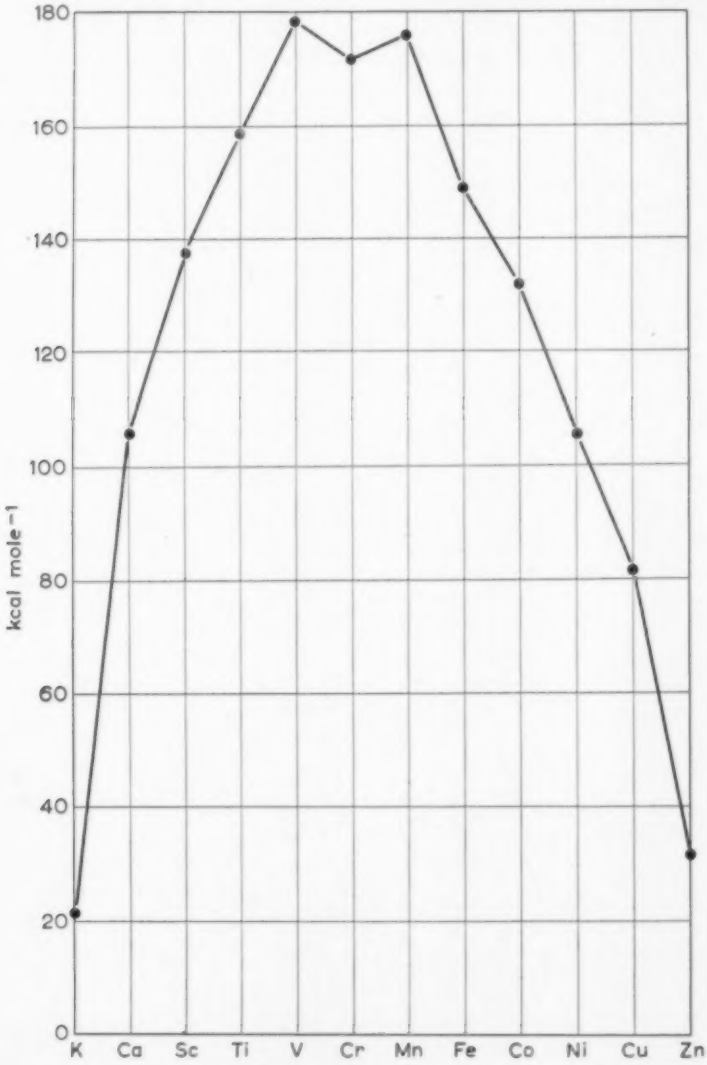


FIG. 2.—Semi-empirical values of $(-p)$ for first transition-series metals, kcal mole$^{-1}$.

as radium). For the minima of the curve lie at three kinds of places—at inert gases, at pseudoinert elements ($d^{10}$ elements: Zn, Cd, Hg), and where the valence-state preparation energy is very large (Mn, Tc). In line with our earlier discussion of the more fundamental quantity $(-p)$, we see from Fig. 3 that in the third period, where there is no dip in the middle of the transition series, the maxima of $\Delta H$ occur midway between the minima—i.e. at tungsten and bismuth. It is interesting that even bromine lies on

the curve. That this is not surprising may be seen by realizing that the number of bonds which can be formed using $4p$ orbitals varies in the same way as $(-p)$ and for much the same reason.

The assumption that in the metal the $s$ and $d$ shells are filled before the $p$ shell starts being occupied seems to become better as we pass down the rows of the periodic table. For it is only because this assumption is not quite true that the Group $2B$ metals are saved from the dreary fate of being inert gases. $\Delta H$ is 31 kcal mole$^{-1}$ for zinc; it decreases to 27 for cadmium and is only 14·5 for mercury. Indeed, one may wonder if eka-mercury—element 112—would be saved at all. The low value for mercury is related to the phenomenon of the inert pair, so important in the chemistry of mercury, thallium, lead, and bismuth.[10]

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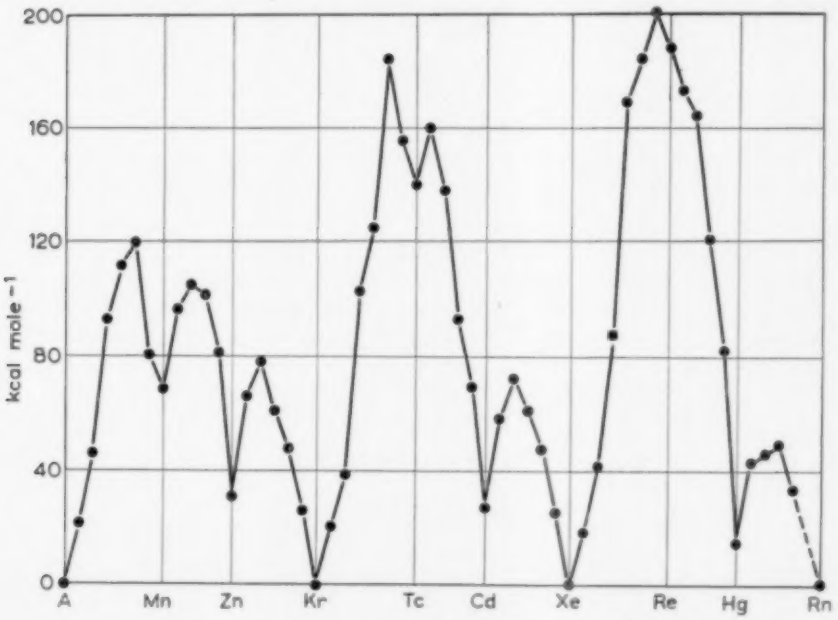


FIG. 3.—Cohesive energies in the three long periods, kcal mole$^{-1}$.

## 4. PHYSICAL SIGNIFICANCE OF THE THEORY

In our explanation of Fig. 1 we have had many assumptions and approximations. Accordingly, it is desirable to pick out the essential physical feature or features of the theory, and this is attempted in this section. We have supposed that, whilst in an atom the valence electrons are coupled as far as possible with parallel spins, in the metal they are coupled antiparallel to electrons from other atoms. In other words, in making a metal from its atoms, we break down the intra-atomic spin couplings and replace them with interatomic ones. This gives rise to two contributions to the cohesive energy, $(-P)$ and $(-p)$ respectively. We calculated $P$ approximately, and supposed $p$ to vary smoothly with atomic number. It seems to me that the essential features of the theory are the form of variation of the two parts $P$ ($= P_1 + P_2$, see equation 4) and $p$. $P_1$ came from experiment, and we calculated $P_2$ in terms of atomic

[10] N. V. SIDGWICK *The Electronic Theory of Valency* p. 179. Oxford University Press (1946).

spectral parameters $B$, $C$, and $G_d$ for the configurations $d^{n-1}s$ with an assumption of perfect pairing. $P_2$ had a steep peak at chromium (Table 1). This, however, was not a result which arrived surprisingly out of the details of the theory. It would be expected by merely glancing at the third column of Table 1 and counting up the number of pairs of electrons with parallel spin in the lowest term of $d^{n-1}s$. $P_2$ represents the amount of spin-coupling broken down in passing to the valence state $M_v$, and there is more spin-coupling which can be broken down in the $^7S$ term of chromium than in any of the other $d^{n-1}s$ ground terms.

As far as the truth of the perfect pairing assumption is concerned, neutron-diffraction experiments[11] suggest that most of the relevant intra-atomic coupling has been broken down in metallic vanadium, chromium, and manganese, although there must be some in ferromagnetic iron and cobalt. We illustrate this by considering iron in a little more detail in the next section. However, although a departure from perfect pairing would affect the numerical values for $P_2$, it would probably not affect the general form of its variation or of that of $P + \Delta H$ in Fig. 2. The form of Fig. 1 is regarded, then, as being mainly a consequence of the varying amounts of exchange energy present in the uncombined constituent atoms rather than of peculiarities of the metals themselves (though not necessarily entirely, as there is still a very small residual dip in the curve of Fig. 2).

Although the details were different, a similar kind of situation arose in the theory of transition metal complexes—that the exchange energy played a fundamental role in determining the heat content of individual complexes. Then the exchange energy in its turn was merely an estimate in terms of an approximate theory of something of rather general significance which finds its expression elsewhere in part of HUND'S rules in atomic spectra (GRIFFITH[4]). This serves to unify the ideas behind my treatment of metals and of their compounds. I feel, however, that the theory of the metals (especially the details) should be regarded as much more tentative than that of their compounds.

## 5. FERROMAGNETIC IRON

We illustrate the breakdown of perfect pairing for the case of ferromagnetic iron, which has the b.c.c. structure. The environment of each metal atom has cubic symmetry. Then the atomic $d$ orbitals of each atom can be chosen so that they fall into two sets belonging, respectively, to the $e_g$ and $t_{2g}$ representations of the cubic group. These orbitals are such that those of one symmetry-type have zero overlap and resonance integrals with all the $\sigma$ orbitals on the eight nearest neighbours, and those of the other symmetry-type with all the $\pi$. The same remark applies to the six next-nearest neighbours. The interactions which are allowed on symmetry grounds are shown in Table 2. A consideration of the detailed form of the functions shows that one would expect them to occur in fact as well, and that the interactions with the next-nearest neighbours should be weaker than those with the neighbours. $\sigma$ bonding is usually stronger than $\pi$ bonding, so we conclude that $e_g$ should interact less strongly than $t_{2g}$ with the rest of the metal.

Now, in certain theories of ferromagnetism it is postulated that two electrons remain on each iron atom with their spins parallel (atomic electrons) and the remainder take part in bonding, forming a "conduction band." Then all the atomic electrons

[11] C. G. SHULL and M. K. WILKINSON *Rev. Mod. Phys.* **25**, 100 (1953).

arrange themselves parallel because of an indirect interaction via the conduction band (ZENER,[12] PAULING[13]). We shall not discuss such theories here, but merely point out two things. The first is that the $e_g$ representation in the b.c.c. structure is a natural place for these atomic electrons, both because it interacts less strongly with the rest of the metal and because it can house just two electrons with parallel spin (I gather that Dr. STEVENS has been independently thinking along somewhat similar

TABLE 2.—BONDING POTENTIALITIES OF $d$ ELECTRONS IN A BODY-CENTRED CUBIC METAL

| Symmetry | Interaction with neighbours | |
|---|---|---|
| | Nearest | Next-nearest |
| $e_g$ | $\pi$ | $\sigma$ |
| $t_{2g}$ | $\sigma$ | $\pi$ |

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lines[14]). The more important for our purpose is that, if we accept this kind of interpretation of ferromagnetism in iron (which differs in detail from that of ZENER[15]), the assumption of perfect pairing is quite untrue for the mutual interaction of these two electrons. If we call the two orbitals of $e_g$ $|0\rangle$ and $|\varepsilon\rangle$, then the b.c.c. iron should be more stable than f.c.c. iron by (see GRIFFITH[3])

$$\begin{aligned} \tfrac{1}{2}K(0\varepsilon) &= 2B + \tfrac{1}{2}C \\ &= 9 \text{ kcal mole}^{-1}, \end{aligned} \tag{9}$$

because the spins are parallel. However, these two electrons no longer take much part in the bonding, so for that reason b.c.c. will be less stable. The small heat of transition between f.c.c. and b.c.c. iron shows these two effects to be practically balanced. In fact, this may be why there is a b.c.c. structure for iron but not for ruthenium or osmium, because these latter elements have larger cohesive, i.e. bonding, energies but smaller electrostatic integrals, i.e. smaller $\frac{1}{2}K(0\varepsilon)$. But our discussion of $p$ assumed that all $d$ electrons took a similar part in the bonding. So for iron we should consider $\Delta H$ for the f.c.c. structure. Quite apart from this theory, however, the nearly equal values of $\Delta H$ seem to be an interesting coincidence. It may be that the theory for the other b.c.c. metals needs some modification in detail too, but for them there is no magnetic evidence against the hypothesis of perfect pairing. We also emphasize that the details of this interpretation of ferromagnetism are peculiarly characteristic of the b.c.c. structure and could not be extended to f.c.c. or h.c.p. metals—in particular to cobalt or nickel (this remark does not apply to the h.c.p. metal gadolinium, for which the 4$f$ electrons may be regarded as "atomic electrons" for different, but well-known, reasons).

*Acknowledgements*—The author is grateful for helpful discussions with Prof. P. GEORGE about the thermodynamic data and with Drs. A. C. HURLEY, L. E. ORGEL, and J. A. POPLE about the theory.

[12] C. ZENER *Phys. Rev.* **81**, 440 (1951).
[13] L. PAULING *Proc. Nat. Acad. Sci.* **39**, 551 (1953).
[14] K. W. H. STEVENS private communication.
[15] C. ZENER *Phys. Rev.* **85**, 324 (1952).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 24 to 27. Pergamon Press Ltd., London

# THE ABSORPTION SPECTRA OF ACIDIFIED MOLYBDATE SOLUTIONS—II

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(*Received* 13 *March* 1956)

**Abstract**—The absorption spectra of sodium molybdate solutions, acidified with perchloric acid, have been studied. A definite acid concentration is shown to exist for maximum optical absorption by the solutions. This optimum acidity is a linear function of the molybdate concentration; the implications of this are discussed.

IN a previous paper[1] the absorption spectra of 0·005 M sodium molybdate solutions that were 0·1 N in hydrochloric, perchloric, sulphuric, and nitric acids were determined over the range 270–330 m$\mu$ and found to be identical. Increase in the concentration of the first three acids to 0·5 N caused no change, but a similar increase in nitric acid concentration changed the form of the curve, suggesting some interaction between nitrate and molybdate. A similar interaction had been suggested by CLARENS[2] in connection with the precipitation of ammonium 12-molybdophosphate.

Although no specific effect of hydrochloric and sulphuric acids was found over this particular wavelength range, there is other evidence that both acids can interact with molybdate in certain circumstances.[3] For this reason, perchloric acid, for which no such interaction has been reported, was used in this series of experiments.

At the rather high acid/molybdate ratios ($<20$) used in the foregoing work, optical density was independent of acid concentration. If, however, the ratio is reduced to values between 3 and 15, extinction becomes acid-dependent. It is this acid-dependence that has been studied.

## EXPERIMENTAL

All extinction measurements were made with a Unicam SP500 spectrophotometer, and all pH measurements with a Pye Universal pH meter, using the methods previously described.[1] However, since wavelengths below 320 m$\mu$ were not required, a tungsten lamp was used throughout; a blue filter was used below 400 m$\mu$. 1-cm silica cells were used; blank solutions contained acid only, of the appropriate concentration.

Fig. 1 shows the optical densities obtained for four different concentrations of molybdate, each with four or five concentrations of acid. Wavelengths were chosen so as to bring the extinction readings within the most accurate range for the instrument.

Using the optimum acidities obtained from Fig. 1, the extinction curve for each concentration of molybdate at the optimum acidity was determined, all readings being taken on the same occasion to minimize temperature variations. The results are shown in Table 1.

Fig. 2 shows the variation of optimum acidity with molybdate concentration.

[1] P. J. COOPE and W. P. THISTLETHWAITE *J. Inorg. Nucl. Chem.* **2**, 125 (1956).
[2] J. CLARENS *Bull. Soc. Chim.* (4) **23**, 147 (1918); **25**, 87 (1919).
[3] K. G. FALK and K. SUGIURA *J. Amer. Chem. Soc.* **37**, 1507 (1915).
R. KUHN *Z. physiol. Chem.* **129**, 64 (1923).
I. NELIDOW and R. H. DIAMOND *J. Phys. Chem.* **59**, 710 (1955).
A. TRAVERS and L. MALAPRADE *Bull. Soc. Chim.* (4) **39**, 1408, 1543 (1926).

## DISCUSSION OF RESULTS

The results in Fig. 1 show clearly that for each molybdate concentration there is a definite acidity for the development of maximum absorption at that wavelength. This is referred to as the "optimum acidity."

It is assumed that the maximum absorption for a given concentration of molybdate occurs at the point of maximum formation of the largest complex. The decrease in the absorption, at acidities above the optimum, is attributed to decomposition of the complex with the formation of mononuclear $Mo^{VI}$ cations. It is noteworthy that CHAUVEAU, SCHAAL, and SOUCHAY[4] have suggested, from variations in the absorption spectra below 230 m$\mu$, that, for 0·01 M molybdate, the formation of $Mo^{VI}$ cations occurs at acid concentrations above 0·05 N; this may be compared with the optimum acidity 0·06 M in the present paper.

The optimum acid concentration should, therefore, correspond to virtual completion of the reaction:

$$n\mathrm{MoO_4^{2-}} + 2n\mathrm{H^+} = (\mathrm{MoO_3})_n + n\mathrm{H_2O}$$

which would imply an equation of the type:

$$\text{opt. acid} = 2[\mathrm{MoO_4^{2-}}] + [\mathrm{H^+}]_{\text{observed}} \qquad (1)$$

from which the pH of the solution at the optimum acidity should correspond to the concentration of added acid minus twice the molybdate concentration. Good agreement between the experimental pH values and those calculated on this basis is evident from Table 1.

TABLE 1

| Series | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $Na_2MoO_4$ concn. (M) | 0·1 | 0·05 | 0·025 | 0·01 | 0·005 |
| $HClO_4$ concn. (M) | 0·44 | 0·23 | 0·12 | 0·06 | 0·04* |
| Wavelength (m$\mu$) | Extinction | | | | |
| 440 | <0·01 | | | | |
| 430 | 0·01 | <0·01 | | | |
| 420 | 0·02 | 0·01 | <0·01 | | |
| 410 | 0·03 | 0·02 | 0·01 | | |
| 400 | 0·06 | 0·03 | 0·02 | <0·01 | |
| 390 | 0·12 | 0·05 | 0·03 | 0·01 | <0·01 |
| 380 | 0·30 | 0·14 | 0·07 | 0·02 | 0·01 |
| 370 | 0·81 | 0·37 | 0·17 | 0·06 | 0·02 |
| 360 | 2·07 | 0·99 | 0·46 | 0·13 | 0·05 |
| 350 | | | 1·16 | 0·32 | 0·11 |
| 340 | | | | 0·74 | 0·24 |
| 330 | | | | 1·53 | 0·52 |
| 320 | | | | | 1·04 |
| pH (observed) | † | † | 1·15 | 1·35 | 1·55 |
| $[H^+]$ (calculated) | 0·24 | 0·13 | 0·07 | 0·04 | 0·03 |
| pH (calculated) | 0·62 | 0·89 | 1·15 | 1·40 | 1·52 |

* Optimum acidity calculated from equation (2). † pH values below 1 are unreliable.

[4] F. CHAUVEAU, R. SCHAAL, and P. SOUCHAY *Compt. Rend.* **240**, 194 (1955).

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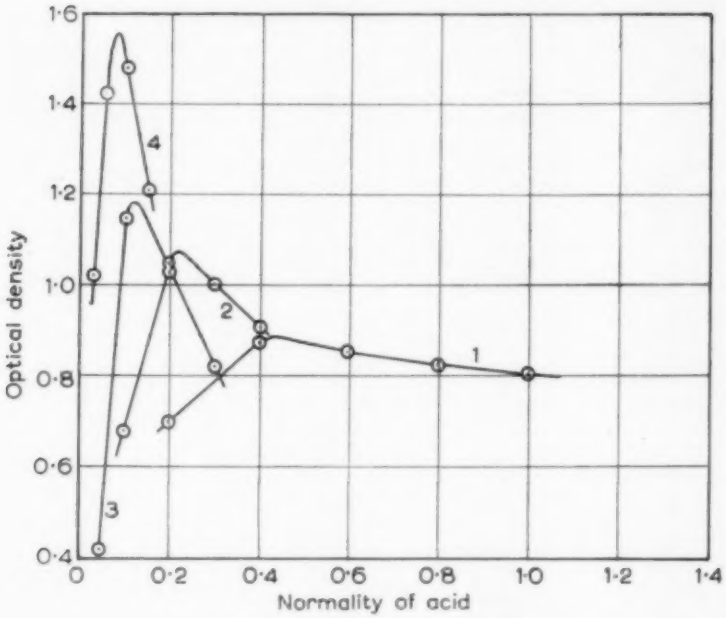


Fig. 1.—1. 0·1 M. $Na_2MoO_4$ at 370 m$\mu$
2. 0·05 M. $Na_2MoO_4$ at 360 m$\mu$
3. 0·025 M. $Na_2MoO_4$ at 350 m$\mu$
4. 0·01 M. $Na_2MoO_4$ at 330 m$\mu$

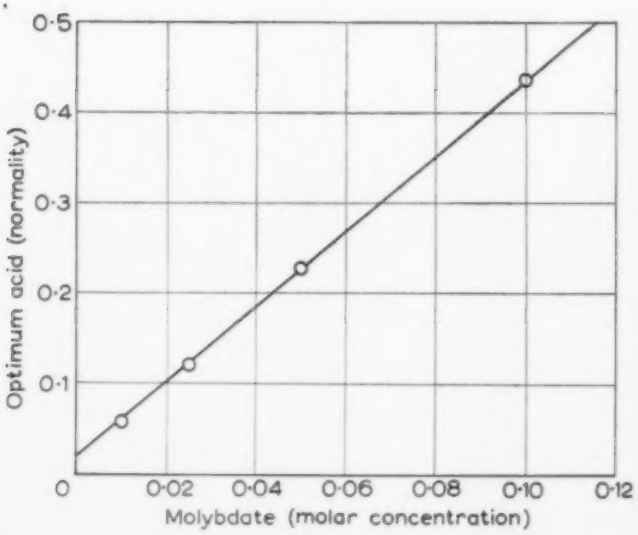


Fig. 2.

The equation for the straight line shown in Fig. 2 was found to be:

$$\text{opt. acid} = 4{\cdot}2[MoO_4^{2-}] + 0{\cdot}02 \tag{2}$$

From this would follow, according to the above argument, that:

$$[H^+]_{\text{observed}} = 2{\cdot}2[MoO_4^{2-}] + 0{\cdot}02 \tag{3}$$

This implies that the residual hydrogen-ion concentration observed in the solution is also a linear function of the original molybdate concentration. It is not clear why such a linear variation should apply, but it is thought that it may be an empirical resultant of the various equilibria existing in the solution. The equilibria envisaged are of the general type:

$$Mo^{VI}\ \text{anions} \overset{OH^-}{\leftrightharpoons} (MoO_3)_n \overset{H^+}{\rightleftharpoons} Mo^{VI}\ \text{cations.}$$

It is conceivable that anions and cations involving different states of aggregation may be involved.

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J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 28 to 37. Pergamon Press Ltd., London

# THE PROTON DISSOCIATION AND HYDROLYSIS OF TRINITRATONITROSYLRUTHENIUM IN AQUEOUS SOLUTIONS

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(*Received* 29 *February* 1956)

**Abstract**—Electrical conductivity measurements on solutions of the trinitratonitrosylruthenium complex in water indicate that it is an acid for which the first dissociation constant has a value of 0·014 mole litre$^{-1}$. The partition coefficient of the complex between solutions in water and in tri-*n*-butyl phosphate (TBP) has been calculated from its observed distribution between these solvents and the degree of dissociation of the complex in aqueous solutions. The hydrolysis of the complex in nitric acid solutions has been shown to occur initially by a first-order rate process with a rate constant $k = 0{\cdot}046$ min$^{-1}$ at 25°C.

## INTRODUCTION

THE behaviour of solutions of the trinitratonitrosylruthenium complex,

$$[RuNO(NO_3)_3(H_2O)_2]\ 2H_2O,$$

in water and in dilute nitric acid has been qualitatively interpreted by FLETCHER *et al.*[1] on the basis of pH measurements, etc., in terms of

(a) a rapid proton dissociation

$$[RuNO(NO_3)_3(H_2O)_2] \rightleftharpoons [RuNO(NO_3)_3OH(H_2O)]^- + H^+ \qquad (1)$$

and (b) a somewhat slower hydrolysis to the dinitrato and lower nitrato complexes, where the first stage is

$$[RuNO(NO_3)_3(H_2O)_2] + H_2O \rightleftharpoons [RuNO(NO_3)_2OH(H_2O)_2] + HNO_3 \qquad (2)$$

In the present work, measurements of the electrical conductivity of solutions of the trinitrato complex in water have been used to calculate the value of the dissociation constant for the equilibrium given in equation (1). The distribution of ruthenium between solutions of the trinitrato complex in water or nitric acid and tributyl phosphate (TBP) is dependent primarily on the concentration of the undissociated complex in the aqueous phase. MARTIN[2] has shown that measurements of this distribution, in aged aqueous solutions of the complex, provide a suitable method for investigating the kinetics of the hydrolysis of the complex; by an extension of his work the order and rate of the first stage of the hydrolysis (equation 2) have been found.

The factors influencing the extraction of organic and inorganic solutes from aqueous solutions into an organic solvent have been reviewed in some detail by IRVING,[3] and it is clear that the observed distribution of a solute between two

[1] J. M. FLETCHER, I. L. JENKINS, F. M. LEVER, F. S. MARTIN, A. R. POWELL, and R. TODD *J. Inorg. Nucl. Chem.* **1**, 378 (1955).
[2] F. S. MARTIN, Ph.D. Thesis, London (1955).
[3] H. M. N. H. IRVING *Quart. Rev.* **5**, 200 (1951).

immiscible phases is dependent on the association or dissociation of the solute in one or both phases. In the present work, in the absence of hydrolysis, a consistent explanation of the observed conductivity and of the distribution of ruthenium is afforded by the postulate that the trinitrato complex dissociates as a weak acid in the aqueous phase.

The nitrosylruthenium complexes belong to the inert rather than to the labile type of transition-metal complexes. In the particular case of the trinitrato complex it has therefore been possible to obtain physical data—its rate of hydrolysis and its partition coefficient with an organic solvent—which are not readily obtainable for the labile nitrato complexes, e.g. uranyl nitrate.

### *Experimental*

The trinitrato complex, labelled with radioactive $Ru^{106}$, was prepared by a method devised by F. S. MARTIN (private communication). This consisted of passing nitrous fumes through a solution of ruthenium tetroxide in carbon tetrachloride followed by extraction of the ruthenium complexes so formed into concentrated nitric acid. This solution was boiled and partially freed from nitric acid by evaporation under infra-red lamps until the solution became viscous, after which it was dried in a vacuum desiccator over phosphorus pentoxide and sodium hydroxide. The solid was found to contain Ru 26·0%, $NO_3$ 47·2%, N 14·5% required for $RuNO(NO_3)_3 \cdot 4H_2O$, Ru 26·1%, $NO_3$ 47·8%, N 14·6%.

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Measurements of the electrical conductivity of solutions made by dissolving the solid trinitrato complex in "Analar" redistilled water, were carried out at 0°C ± 0·05° with a Mullard conductivity bridge (Type E-7566) and Mullard dip-type electrodes (Type E-7591B). The cell constant was 1·50 and the accuracy of measurement ±2%. Measurements were made at frequent intervals over a period of 45 min, and a sharp increase in conductivity during the first 10–12 min was noted, after which a steady increase with time was observed. As the solution was made by dissolving the solid trinitrato complex in water, an initial increase in conductivity would be expected as the material dissolved. Thereafter, owing to hydrolysis of the complex, there was a linear increase, as shown in Fig. 1, where the observed conductivity is plotted against time. Extrapolation of the linear portion to zero time gave the value of the conductivity at zero time, from which $K$, the specific conductivity, and $\Lambda$, the equivalent conductivity, were calculated. The initial curvature was not the same in each case; this is because different amounts of the solid complex were taken and the physical form of the solid differed, small flakes dissolving rapidly while larger aggregates took appreciably longer to dissolve.

To obtain distribution coefficients, weighed amounts of the solid trinitrato complex were dissolved in water or nitric acid at the requisite temperature and aliquots taken at timed intervals for immediate equilibration with an equal volume of a 30% (v/v) TBP in kerosene (30% TBP). Transfer of nitric acid from the aqueous into the organic phase was eliminated by the use of TBP previously equilibrated with an aqueous solution of nitric acid of the requisite concentration. For the distribution measurements, the stirring time was 30 sec, and, after stirring, the mixtures were immediately centrifuged and the phases separated. The rhodium $\gamma$ activity (derived from $Ru^{106}$) present in each phase was counted with a $\gamma$ scintillation counter fitted with a 20 mg/cm² lead-aluminium absorber. Samples were prepared for counting within 5 min of phase separation.

## THE PROPERTIES OF SOLUTIONS OF THE TRINITRATO-NITROSYLRUTHENIUM COMPLEX IN WATER

### *The Dissociation of the Complex in Water*

The equivalent conductivities (at 0°C) of solutions of the trinitrato complex in water at zero time of ageing are given in Table 1. An approximate value of $\Lambda_0$, the equivalent conductivity at infinite dilution, was obtained from these results by

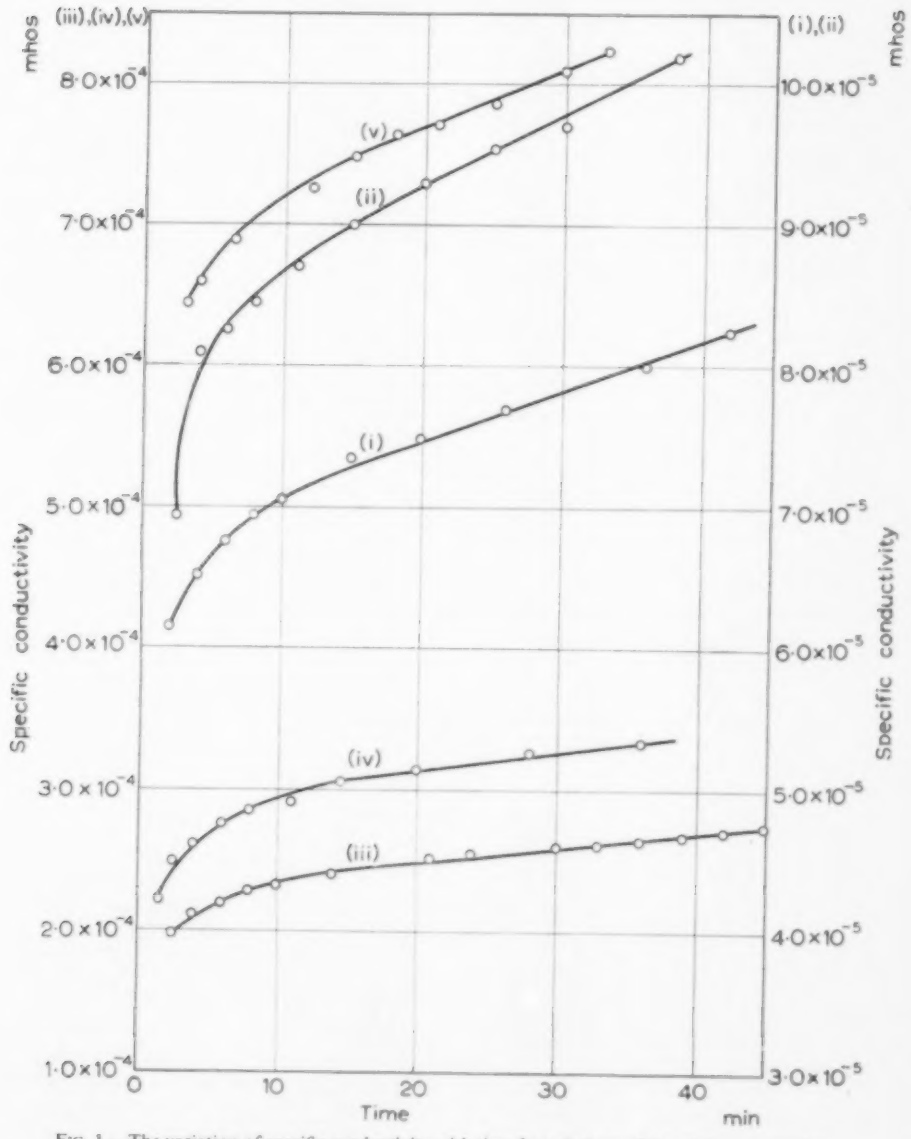


FIG. 1.—The variation of specific conductivity with time for solutions of the trinitrato complex in water at 0°C.
(i) $2{\cdot}60 \times 10^{-4}$ M
(ii) $3{\cdot}22 \times 10^{-4}$ M
(iii) $9{\cdot}00 \times 10^{-4}$ M
(iv) $1{\cdot}23 \times 10^{-3}$ M
(v) $3{\cdot}38 \times 10^{-3}$ M
Curves (i) and (ii): right-hand scale.
Curves (iii), (iv), and (v): left-hand scale.

TABLE 1.—THE DISSOCIATION OF TRINITRATONITROSYLRUTHENIUM DERIVED FROM THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF IT IN WATER

| Concentration (g-eq/litre) | $\Lambda$ (ohm$^{-1}$) | $K_1$ mole/litre$^{-1}$ | $\gamma_\pm$* | $\alpha$* |
|---|---|---|---|---|
| $1{\cdot}0 \times 10^{-4}$ | — | — | 0·989 | 0·993 |
| $2{\cdot}60 \times 10^{-4}$ | 260 | 0·018 | 0·983 | 0·983 |
| $3{\cdot}22 \times 10^{-4}$ | 258 | 0·014 | 0·981 | 0·979 |
| $9{\cdot}00 \times 10^{-4}$ | 251 | 0·019 | 0·969 | 0·946 |
| $1{\cdot}23 \times 10^{-3}$ | 235 | 0·009 | 0·964 | 0·930 |
| $3{\cdot}38 \times 10^{-3}$ | 205 | 0·009 | 0·947 | 0·846 |

* Calculated from the mean value $K = 0{\cdot}014$ mole litre$^{-1}$.

application of OWEN's method of extrapolation.[4] A more sensitive method[5] was then applied and the value $\Lambda_0 = 265$ ohm$^{-1}$ was obtained.

It is known that dissociation of the complex into a hydrogen ion and a complex anion occurs in water;[1] subtraction of the limiting ionic mobility of the hydrogen ion (240 ohm$^{-1}$ at 0°C) from $\Lambda_0$ gives a value for the limiting ionic mobility of the anion $[RuNO(NO_3)_3OH\ H_2O]^-$ of 25 ohm$^{-1}$ at 0°C.

For different concentrations, values of $\alpha$, the degree of dissociation of the complex, may be calculated from the conductivity data by the usual method of successive approximations; and values of $\gamma_\pm$, the mean ionic activity coefficient of the electrolyte, may be calculated from DAVIES's semi-empirical activity coefficient formula:[6]

$$-\log \gamma_\pm = 0{\cdot}488\, Z_+ + Z_- \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0{\cdot}2I\right],$$

where $I$ is the ionic strength of the solution, and $Z_+$ and $Z_-$ are the charges on the cation and anion respectively. Individual values of $K_1$, the first proton dissociation constant for the trinitrato complex, calculated from the relationship

$$K_1 = \alpha^2 C \gamma_\pm^2 / (1 - \alpha)\gamma_{AB}$$

where $\gamma_{AB}$, the activity coefficient of the undissociated complex, is taken as unity, are given in Table 1 together with values of $\alpha$ and $\gamma_\pm$ recalculated using the mean value of $K_1$ (0·014 mole litre$^{-1}$).

*The Distribution of the Trinitrato Complex between Water and TBP*

As a result of the hydrolysis of the trinitrato complex in water, the observed distribution coefficients (org./aq.) of ruthenium between solutions of the complex in water and an immiscible solvent (e.g. 30% TBP) vary with the age of the solution. Therefore, in order to obtain distribution coefficients which are not affected by this hydrolysis, it is necessary to extrapolate the experimental results to zero time. Since the hydrolysis is rapid, even at 0°C (see below), and as the solid takes a finite time to dissolve, the extrapolated values are rather sensitive to the method of extrapolation employed. Two methods have been used:

[4] B. B. OWEN *J. Amer. Chem. Soc.* **61**, 1393 (1939).
[5] L. ONSAGER *Physikal. Z.* **28**, 277 (1927).
[6] C. W. DAVIES *J. Chem. Soc.* 2097 (1938).

(i) The reciprocal of the observed distribution coefficient has been plotted against time, giving $D_0^1$ the extrapolated distribution coefficient at zero time, and

(ii) the reciprocal of the observed concentration of ruthenium in the TBP phase has been plotted against time, giving, by calculation, another extrapolated distribution coefficient, $D_0^2$.

These methods are illustrated in Fig. 2, and values of $D_0^1$ and $D_0^2$ are given in Table 2.

TABLE 2.—CALCULATION OF THE PARTITION COEFFICIENT OF THE TRINITRATO COMPLEX BETWEEN WATER AND 30% TBP

| Initial ruthenium concentration (g-eq/litre) | $D_0^1$ | $D_0^2$ | $K_T^1$ | $K_T^2$ | $K_T$ |
|---|---|---|---|---|---|
| $2{\cdot}5 \times 10^{-4}$ | 1·0 | 2·4 | 109 | 400 | 243 |
| $1{\cdot}13 \times 10^{-3}$ | 2·0 | 5·2 | 80 | 400 | 212 |
| $3{\cdot}66 \times 10^{-3}$ | 6·0 | 7·6 | 178 | 271 | 227 |
| $1{\cdot}06 \times 10^{-2}$ | 14·3 | 11·4 | 333 | 219 | 272 |

The dependence of $D_0$ on the initial ruthenium concentration is explained by the variation in the degree of dissociation of the complex. The electrical conductivity of solutions of the trinitrato complex in 30% TBP saturated with water was found to be negligible, i.e. the complex exists in this solvent as the un-ionized form. It is therefore justifiable to assume that the distribution of ruthenium between a solution in water and 30% TBP is governed by the concentrations of the un-ionized complex in the two phases such that $\frac{\text{[un-ionized complex] in TBP}}{\text{[un-ionized complex] in water}}$ is a constant, $K_T$, the partition coefficient of the complex.

In the ideal case, with no hydrolysis, and with equal volumes of the two phases, $K_T$ may be calculated as follows. Let $C$ be the initial concentration of the trinitrato complex in the aqueous phase and let $D_0$ be the value of the distribution coefficient found by extrapolation to zero time. Then the total concentration of nitrosylruthenium (trinitrato and mononuclear hydrolysis products) in the aqueous phase when partition equilibrium has been established is $C/(1 + D_0)$; with the appropriate values of $\alpha$ for this concentration, then $K_T = D_0/(1 - \alpha)$. From this relationship, values of $K_T^1$ and $K_T^2$, calculated respectively from the extrapolated values $D_0^1$ and $D_0^2$, are given in Table 2; values of $\alpha$ at a ruthenium concentration of $C/(1 + D_0)$ were in each case obtained by interpolation from the data given in Table 1.

The calculated values $K_T^1$ and $K_T^2$ show distinct trends in opposite directions, the true value probably lying between these extremes; using for each initial concentration of ruthenium the mean value of $D_0^1$ and $D_0^2$, reasonably constant values for $K_T$ are obtained with a mean value of 240. With ruthenium concentrations $> 1 \times 10^{-2}$ M, the uncertainty in $D_0^1$ and $D_0^2$ is considerably increased, as the nitric acid liberated during hydrolysis has a marked effect on the ionization of the complex (see below). An approximate value for $K_T$ of 300 has been derived by

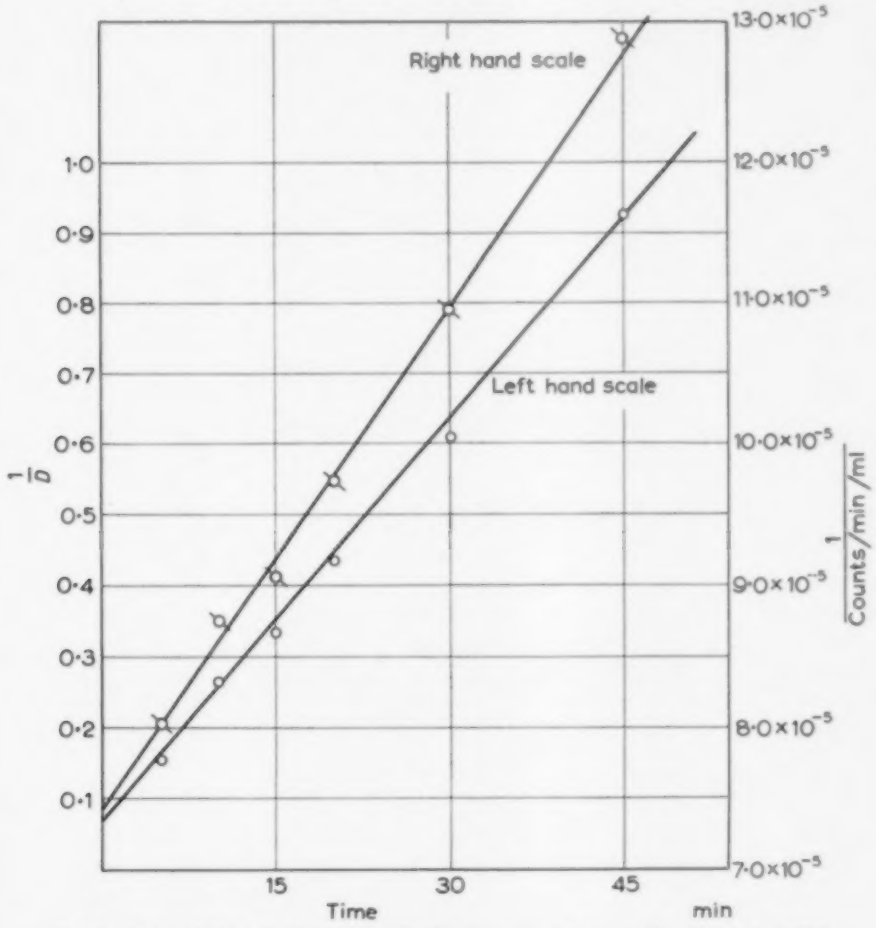


FIG. 2.—Extrapolation of ruthenium distribution measurements to zero time to give $D_0$ at 0°C.
Alternative extrapolations:

I Plot of $\frac{1}{D}$ where $D$ is $\frac{[\text{Ru}]\ \text{org.}}{[\text{Ru}]\ \text{aq.}}$

II Plot of $\frac{1}{[\text{Ru}]\ \text{org.}}$ expressed as $\frac{1}{\text{counts/min/ml}}$ in TBP phase.

Total ruthenium concentration $= 1{\cdot}06 \times 10^{-2}$ M
$= 14{,}662$ counts/min/ml.

P. G. M. BROWN (private communication) from different experiments; in view of the uncertainty of our extrapolations, the agreement is satisfactory.

*The Hydrolysis of the Trinitratonitrosylruthenium Complex in Water.*

A quantitative study of the hydrolysis of the trinitrato complex in water by a partition method is complicated by the following factors:

(i) The distribution of the complex between water and TBP has been shown to depend on the degree of dissociation of the complex.

(ii) As a result of (i), not only does the observed distribution vary with the initial ruthenium concentration, but as the concentration of the trinitrato complex is continually decreasing due to hydrolysis, this variation will no longer be simple.

(iii) Hydrolysis is known to proceed beyond the stage shown in equation (2), the final products being polynuclear species. Thus the successive hydrolyses may be represented:

Trinitrato complex → Dinitrato complex → Mononitrato complex → Polynuclear species.

(iv) The hydrolysis products (other than the polynuclear species) have low but finite partition coefficients, and although their extraction may be ignored in the early stages of hydrolysis, this is no longer the case when their proportions are relatively high.

(v) The hydrolysis is fast even at 0°C; at 25°C approximately 50% of the trinitrato complex is hydrolysed in 3 min.

Some results illustrating the combined effects of (i) to (v) are shown in Table 3, where data on the distribution of ruthenium between water and 30% TBP at 0°C are presented.

TABLE 3.—THE DISTRIBUTION OF RUTHENIUM BETWEEN EQUAL VOLUMES OF WATER AND 30% TBP at 0°C.

| Initial concentration of trinitrato complex (M) | $D_0$* | $D$ (org/aq) | |
|---|---|---|---|
| | | 6-min ageing | 15-min ageing |
| $2{\cdot}5 \times 10^{-4}$ | 1·7 | 0·81 | 0·63 |
| $1{\cdot}13 \times 10^{-3}$ | 3·6 | 1·43 | 0·97 |
| $3{\cdot}66 \times 10^{-3}$ | 6·8 | 3·1 | 1·9 |
| $1{\cdot}06 \times 10^{-2}$ | 12·8 | 5·5 | 2·8 |

* $D_0$ is the mean of the two values taken from Table 2 for the distribution coefficient at zero time.

## THE HYDROLYSIS OF THE TRINITRATONITROSYLRUTHENIUM COMPLEX IN NITRIC ACID SOLUTIONS

### *The Distribution of the Trinitrato Complex between Nitric Acid and 30% TBP*

It has been shown above that with solutions of the complex in water, the distribution of ruthenium between the aqueous phase and 30% TBP is dependent on the degree of dissociation of the complex. In nitric acid the proton dissociation of the complex is repressed and therefore at any given nitric acid concentration (above a certain minimum) and in the absence of hydrolysis, the distribution coefficient should be constant irrespective of ruthenium concentration. For example, in contrast to the results in Table 2, $D_0$ was found to be 15·1 and 15·0 at 0°C, with 0·75 M $HNO_{3aq.}$ for solutions made by dissolving a preparation of the trinitrato complex such that the concentrations of ruthenium were $1{\cdot}05 \times 10^{-2}$ and $1{\cdot}14 \times 10^{-3}$ M respectively. The partition coefficient of the trinitrato complex between 0·75 M nitric acid and 30% TBP is 120,[1] but its value is very sensitive to the presence of less extractable species; the presence of $\leqslant 5\%$ of the dinitrato complex in the particular preparation used is sufficient to explain the discrepancy between the values of 120 and 15. At higher concentrations of nitric acid, $D_0$ is lower as a result of competition for the solvent between the ruthenium complexes and nitric acid, which is also extracted by TBP, i.e. $D_0$ is a function of the free TBP concentration. The temperature dependence of $D_0$ is such that the ratio of the values at 0° and 25°C is 1·86.

### *The Hydrolysis of the Trinitrato Complex in Nitric Acid Solutions*

The partition coefficient of the trinitrato complex between TBP and aqueous

nitric acid solution is known to be considerably greater than those of the hydrolysis products (values 20 or more times greater are given by FLETCHER *et al.*).[1] Consequently, it is possible to follow the kinetics of the hydrolysis by measuring the decrease in extractability of ruthenium with time into 30% TBP. During the initial stages of the hydrolysis the extraction of the hydrolysis products may be neglected; the concentration of ruthenium in the organic phase is then a linear function of the concentration of the unhydrolysed trinitrato complex in the aqueous phase. The variation of the extractability of ruthenium with time into 30% TBP was therefore studied,

(i) at the same nitric acid concentration (0·7–0·8 M) for different initial concentrations of the complex. In this case measurements were carried out at 0°C ± 0·05°, 25°C ± 0·01°, and 35°C ± 0·05°; and

(ii) for a constant initial concentration of the complex over a range of nitric acid concentrations from 0·08 to 4·08 M $HNO_3$.

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The method of GUGGENHEIM[7] was employed to interpret the kinetic results. Samples were taken at known time-intervals $t_1$, $t_2$, etc., from solutions of the complex in nitric acid for immediate equilibration with 30% TBP. The number of $\gamma$ counts in the organic phase was plotted against time, and values of $r_i$, the number of counts at time $t_i$, and of $R_i$, the number at time $t_i + T$ (where $T$ is a fixed time-interval, say 5 or 10 min), were interpolated from a smooth curve drawn through the points. Plots of log $(R_i - r_i)$ against $t_i$ gave straight lines indicative of a first-order reaction; $k$, the rate constant, was obtained by equating the slopes of the lines to $-0{\cdot}4343k$. Smaller values than are usual of $T$ in relation to the half-time have been used, as there is evidence that hydrolysis eventually proceeds at least as far as the mononitrato complex.[1] Fig. 3 shows the results obtained in a typical experiment, and values of the rate constants $k'$, calculated with $T = 5$ or 6 min, and $k''$, calculated with $T = 10$ or 12 min, are given in Table 4.

TABLE 4.—THE RATE CONSTANT FOR THE HYDROLYSIS OF THE TRINITRATO COMPLEX IN NITRIC ACID

| [Ru] (M) | [$HNO_3$] (M) | $k'$ ($min^{-1}$) | $k''$ ($min^{-1}$) | Temp. (°C) |
|---|---|---|---|---|
| $5{\cdot}75 \times 10^{-4}$ | 0·08 | 0·057 | 0·054 | 25 |
| $3{\cdot}72 \times 10^{-4}$ | 0·72 | 0·057 | 0·060 | 25 |
| $1{\cdot}12 \times 10^{-3}$ | 0·72 | 0·047 | 0·057 | 25 |
| $3{\cdot}56 \times 10^{-4}$ | 0·80 | 0·046 | 0·044 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 0·77 | 0·042 | 0·042 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 0·77 | 0·050 | 0·049 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 0·77 | 0·043 | 0·046 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 1·37 | 0·039 | 0·038 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 2·00 | 0·051 | 0·042 | 25 |
| $5{\cdot}75 \times 10^{-4}$ | 4·05 | 0·037 | 0·031 | 25 |
| $1{\cdot}05 \times 10^{-3}$ | 0·72 | 0·0189 | — | 0 |
| $1{\cdot}14 \times 10^{-3}$ | 0·72 | 0·0182 | — | 0 |
| $5{\cdot}75 \times 10^{-4}$ | 0·77 | 0·060 | — | 35 |

[7] E. A. GUGGENHEIM *Phil. Mag.* **2**, 538 (1926).

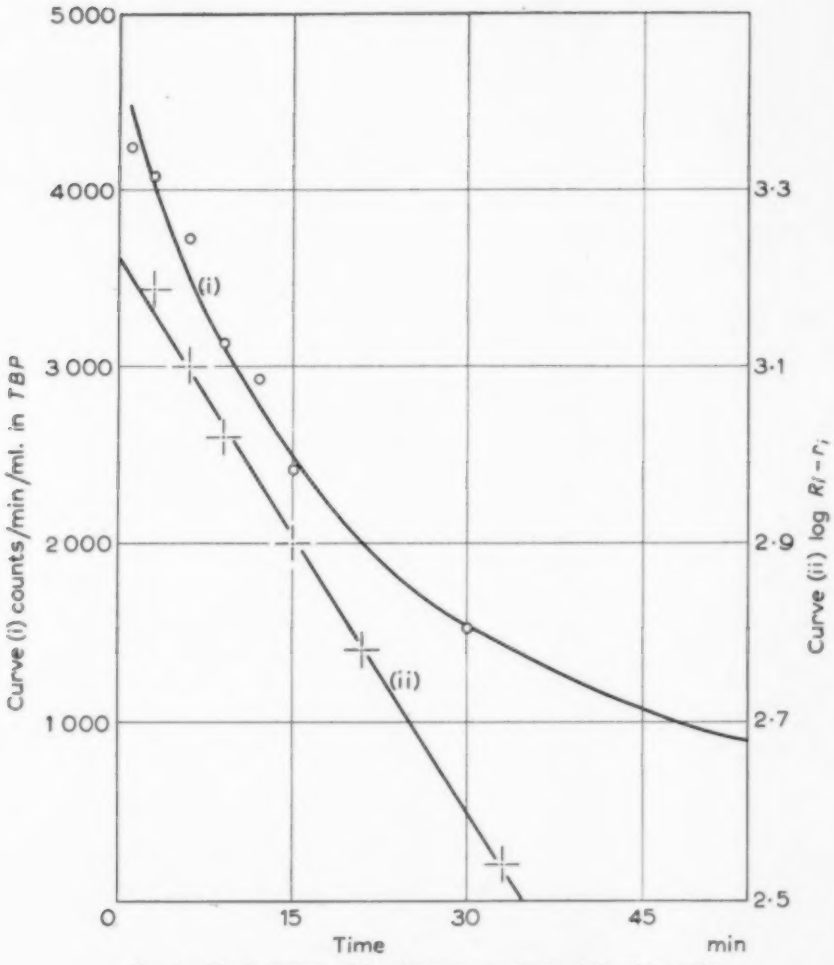


FIG. 3.—The hydrolysis of the trinitrato complex in nitric acid at 25°C.
$5{\cdot}75 \times 10^{-4}$ M ruthenium in 0·77 N $HNO_3$
Curve (i)—A plot of the $\gamma$ counts/min/ml in the TBP phase against time.
Curve (ii)—Plot of log $R - r_t$ against time.

The close agreement between the mean values at 25°C for $k'$ (0·046 $min^{-1}$) and for $k''$ (0·047 $min^{-1}$) for concentrations of ruthenium from $3{\cdot}7 \times 10^{-2}$ to $5{\cdot}75 \times 10^{-5}$ M in 0·7–0·8 M nitric acid is good evidence for the occurrence of a first-order rate process. Further evidence for this is afforded by the fact that the observed distribution coefficients of ruthenium between solutions in 0·72 M nitric acid and 30% TBP are identical at any given time of ageing irrespective of the initial ruthenium concentration, e.g. after $9\frac{1}{4}$ min ageing (at 25°C) $D_{Ru} = 1{\cdot}00$ and 1·01 for initial ruthenium concentrations of $3{\cdot}7 \times 10^{-2}$ M and $1{\cdot}12 \times 10^{-3}$ M respectively.

The fact that the rate of hydrolysis is independent of nitric acid concentration over the range 0·08 to 4 M indicates that there is no primary salt effect ($Z_A + Z_B =$ zero, where $Z_A$ and $Z_B$ are the charges on the reacting species) and that the reaction that occurs is of the type

$$[RuNO(NO_3)_3(H_2O)_2]^0 + H_2O \rightarrow [RuNO(NO_3)_2OH(H_2O)_2] + HNO_3 \quad (3)$$

or $$[RuNO(NO_3)_3OH\ H_2O]^- + H_3O^+ \rightarrow [RuNO(NO_3)_2OH(H_2O)_2] + NO'_3 + H^+. \quad (4)$$

Provided, as is likely, that the dissociation is a mobile one, there is no possibility of distinguishing between the two mechanisms, but the first mechanism is the simpler to envisage. Further hydrolytic reactions, such as that for the dinitrato to mononitrato complex, are involved:

$$H_2O + [RuNO(NO_3)_2OH(H_2O)_2] \rightleftharpoons [RuNO(NO_3)(OH)_2(H_2O)_2] + HNO_3 \quad (5)$$

Since the amount of the dinitrato complex extracted is negligible in the period of time for which the rate constants were determined, the observed rate depends on the disappearance of the trinitrato complex, i.e. is that for the hydrolysis of the trinitrato complex, as shown in equation (3) or (4).

The temperature coefficient of the observed hydrolysis, calculated from the results in Table 4 at 0°, 25°, and 35°C, leads to the abnormally low value of approximately 6000 cal per mole for the energy of activation. This would indicate a frequency factor ($A$) of only $10^3$ $min^{-1}$ compared with the usual value of around $10^{15}$ $min^{-1}$ for first-order reactions occurring at measurable rates at room temperature.

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J. Inorg. Nucl. Chem., 1956, Vol. 2, pp. 38 to 48. Pergamon Press Ltd., London

# COBALT, NICKEL, AND COPPER SALICYLALDOXIME COMPOUNDS AT HIGH pH's: BEHAVIOUR, COMPOSITION, AND STRUCTURE

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**Abstract**—The only cobalt complex which is formed at pH's 6–8 is soluble and has the composition $[Co_2^{III}(SAO)_3]^0$.

With nickel, an insoluble complex $[Ni(SAO)_2]^0$ is formed quantitatively between pH = 6 $\leqslant$ 12. At pH $\geq$ 12 it is abruptly and completely transformed into the soluble complex $[Ni(SAO)_2]^{2-}$. $K = [Ni^{2+}][SAO]^2/[Ni(SAO)^{2-}_2] = 1{\cdot}7 \times 10^{-4}$.

With copper, the insoluble complex $[Cu(SAO)_2]^0$ is quantitatively formed between pH 3–10, and it is completely and abruptly transformed into $[Cu(SAO)_2]^{2-}$ which is soluble, at pH $\geq$ 11. $K = [Cu^{2+}][SAO^{2-}]^2/[Cu(SAO)_2^{-2}] = 6{\cdot}4 \times 10^{-5}$.

Ammonia does not interfere with the soluble complexes.

## INTRODUCTION

ALTHOUGH the compounds formed between various cations and salicylaldoxime (= SAO) have been studied from the analytical standpoint by different workers,[1] some fundamental problems remain to be solved. There is no clear picture of the composition and structure of the salicylaldoximates which are obtained under different working conditions. In particular, there is no clear conception of the interrelation between the *insoluble* compounds which are obtained at lower pH's and the *soluble* compounds which are formed at high pH's. The composition, behaviour, and stability of the latter are unknown.[2] A study of these latter compounds may cast some light on the different SAO-structures which participate in the complex formation.

Our intention was to investigate the soluble compounds, spectrophotometrically, and at the same time to carry out a parallel study of the insoluble compounds obtained, using the heterometric method (photometric study of suspensions), which was developed by the first author with co-workers.[3] This paper presents the results of such a study with some coloured bivalent cations.

[1] F. EHRAIM *Ber.* **64**, 1215 (1931)
I. F. FLAGG and N. H. FURMAN *Ind. Eng. Chem., Anal. Ed.* **12**, 529 (1940)
F. FEIGL and A. BONDI *Ber.* **64**, 2819 (1931)
[2] F. FEIGL *Specific, Selective, Sensitive Reactions*, Academic Press, N.Y. 1949.
[3] M. BOBTELSKY and B. GRAUS *J. Amer. Chem. Soc.* **75**, 4172 (1953); *ibid* **76**, 1536 (1954); *ibid* **77**, 1990 (1955).
M. BOBTELSKY and B. GRAUS *Bull. Res. Council Israel* **3**, 82-88 (1953); *ibid*, **4**, 69 (1954)
M. BOBTELSKY and B. GRAUS *Anal. Chim. Acta* **9**, 163 (1953); *ibid*, **11**, 253 (1954)
M. BOBTELSKY and I. BAR-GADDA *Bull. Soc. Chim.* 276, 382, 687, 819 (1953)
M. BOBTELSKY and I. BAR-GADDA *Anal. Chim. Acta* **9**, 168, 446, 525 (1953)
M. BOBTELSKY and Y. WELWART *Anal. Chim. Acta* **9**, 281, 374 (1953); *ibid* **10**, 151, 156, 459, 464 (1954)
M. BOBTELSKY and M. BIHLER *Anal. Chim. Acta* **10**, 260 (1954)
M. BOBTELSKY and M. HALPERN *Anal. Chim. Acta* **11** 84, 188 (1954)
M. BOBTELSKY and S. KERTES *J. Appl. Chem.* **4**, 419 (1954); *ibid*, **5**, 125, 675 (1955)
M. BOBTELSKY and E. JUNGREIS *Anal. Chim. Acta* **12**, 248, 263, 351, 562 (1955); **13**, 72, 449 (1955)
M. BOBTELSKY and E. JUNGREIS *Bull. Soc. Chim.* 1161 (1955)
M. BOBTELSKY *Anal. Chim. Acta* **13**, 172 (1955)
M. BOBTELSKY and J. EISENSTADTER *Anal. Chim. Acta* **14**, 89, 186 (1956)
M. BOBTELSKY and R. RAFAILOFF *Anal. Chim. Acta* **14**, 247, 339 (1956)
M. BOBTELSKY and A. BEN-BASSAT *Anal. Chim. Acta* **14**, 344 (1956).

## EXPERIMENTAL

For the study of the coloured solution, the Beckman DU spectrophotometer was used. Some photometric titrations were made with the "Heterometer."[3] For the study of reactions in suspensions the heterometer constructed by the first author, was used. pH-measurements were made with the Beckman pH-meter model H2. A set of Beckman glass and saturated calomel electrodes were used. Both electrodes were immersed in the solution during the titrations and other experiments.

The reagents used were all Baker analytical or CP reagents. The salicylaldoxime was a 'Light & Co.' reagent. A solution of this was prepared in water. Higher SAO-concentrations were obtained by dissolving SAO in alcohol.

## RESULTS

### 1. *Cobalt Salicylaldoximate*

*A pH-photometric study.* Fig. 1 presents a series of photometric titrations (curves 1–3) carried out by the addition of either NaOH or $HNO_3$ to a buffered solution which contained a fixed amount of cobalt nitrate and an excess of SAO. The composition of the experiments may be taken from the figure. During these titrations, the pH of the solution continuously changes. The pH's may be taken for each point from the corresponding dashed "*a*"-curves. (The same numeration of the curves was used both for the heterometric and for the pH-titration, but in the latter case the dashed curves are designated as "*a*"-curves.) As no suitable filter could be found, these photometric titrations were therefore carried out with the heterometer, but without filter.

In addition, we present experiment 4 (curve 4), which is similar to experiment 3 (as to the pH working conditions) except that the measurements were made in cells using Beckman DU spectrophotometer at the wavelength 600 m$\mu$. At this wavelength (see Fig. 2) the absorption of the Co-SAO complex is considerable, while the absorption of SAO is equal to zero. Under all pH-conditions a *soluble* complex only was obtained.

Curve 1 (Fig. 1) shows that the main complex formation begins at pH $\sim$ 6 and is complete at pH $\sim$ 8. Increases in the pH have no further influence even at pH $\sim$ 12. Practically identical results are obtained when working with ammonia buffer (curve 3). *This means that ammonia does not interfere with the complex formation.* Curve 2 shows the results obtained when the titration began at high pH. The complex, once formed, is stable at lower pH's. As the pH-density measurements at 600 m$\mu$ (with the spectrophotometer) show (curve 4), the complex formation may already be complete even at pH $\sim$ 7.

The following experiments were carried out in order to obtain information about the changes with time in the absorption at 600 m$\mu$ of $Co(NO_3)_2$-SAO mixtures at high pH's. The same experiments were carried out in open and closed bottles at room temperature.

The composition of the experiments was:

(1) 4 ml $Co(NO_3)_2$ 0·005 M + 8 ml SAO 0·005 Malc. + 5 ml $H_3BO_3$ 0.2 M + 4·4 ml NaOH 0·2 N.

(2) 4 ml $Co(NO_3)_2$ 0·005 M + 12 ml SAO 0·005 Malc. + 5 ml $H_3BO_3$ 0·2 M + 4·4 ml NaOH 0·2 N

The pH of the solutions was 10·0.

In all cases the measured absorption values became constant after 15 to 30 min, and they then remained unchanged. In the experiments in open bottles, the end values

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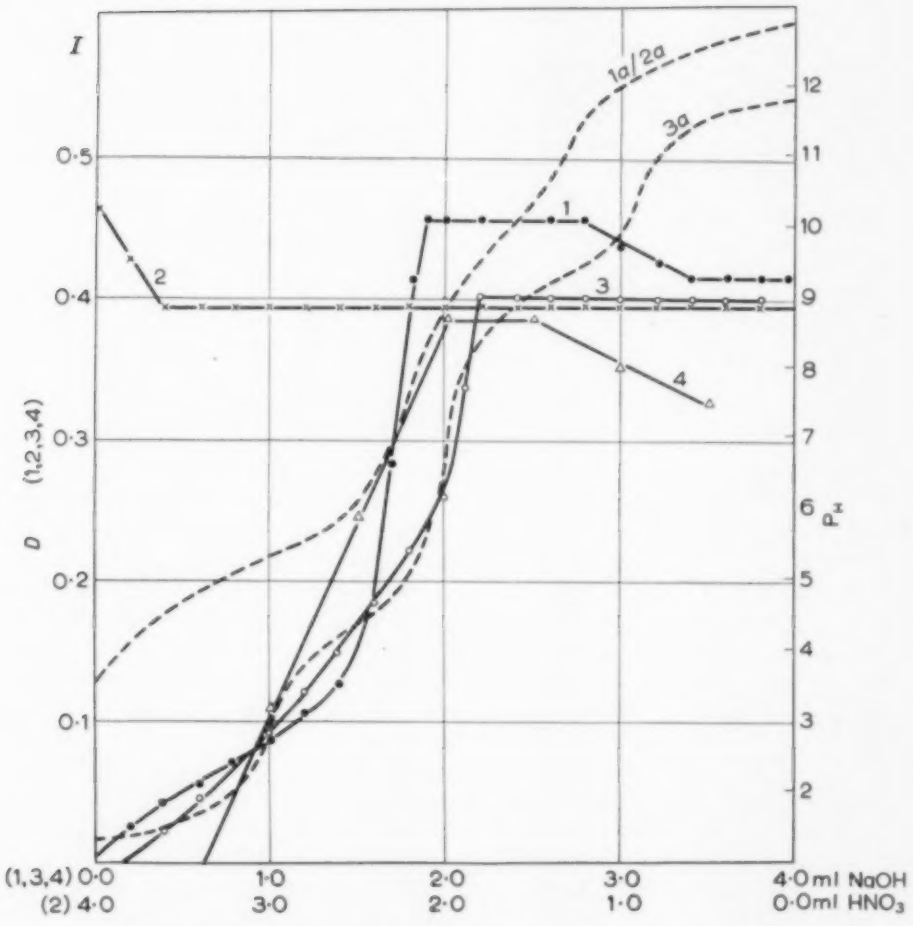


FIG. 1.
1. 3 ml $Co(NO_3)_2$ 0·005 M + 1·5 ml $CH_3COOH$ 0·4 N + 3 ml $H_3BO_3$ 0·2 N + 2·5 ml SAO 0·02 M + 10 ml $H_2O$ + $x$ ml NaOH 0·4 N.
2. 3 ml $Co(NO_3)_2$ 0·005 M + 1·5 ml $CH_3COOH$ 0·4 N + 3 ml $H_3BO_3$ 0·2 N + 2·5 ml SAO 0·02 M + 4 ml NaOH 0·4 N + 6 ml $H_2O$ + $x$ ml $HNO_3$ 0·4 N.
3. 3 ml $Co(NO_3)_2$ 0·005 M + 1 ml $HNO_3$ N + 1 ml $CH_3COOH$ N + 2 ml $NH_4NO_3$ M + 4 ml SAO 0·01 M + 9 ml $H_2O$ + $x$ ml NaOH N.
4. 4 ml $Co(NO_3)_2$ 0·005 M + 1 ml $HNO_3$ N + 1 ml $CH_3COOH$ N + 2 ml $NH_4NO_3$ M + 4 ml SAO 0·01 M + $x$ ml NaOH N + $(8 - x)$ ml $H_2O$. $\lambda = 600$ m$\mu$.
1a–4a : pH curves.

were a few per cent higher than in the corresponding experiments in closed bottles. In both cases there was sufficient air in the solution to oxidize the Co(II) to Co(III).

Based on these results, all the spectrophotometric measurements with Co-SAO mixtures were carried out after they had stood for more than half an hour in closed bottles.

Fig. 2 shows the spectra of the cobalt-SAO complex and SAO blanc at pH 10·0. From absorption spectra which were obtained using different amounts of cobalt, it could be ascertained that the optical densities obtained at different wavelengths

were proportional to the amount of cobalt in solution. No maximum density is obtained at lower wavelengths, and the density rises continuously in the visible spectrum as the wavelength decreases. This shows that the spectrum of Co-SAO mixtures is different from the spectra of other bivalent Co(II)-complexes at high pH's.

In order to study the composition of the complex obtained, photometric titrations were carried out at pH = 10, using either $NH_3/NH_4NO_3$ or borate buffer solutions. The composition of these experiments and the results obtained may be seen in Fig. 3. The titrations were carried out with the DU spectrophotometer at wavelengths 450 m$\mu$, 500 m$\mu$, and 600 m$\mu$. In all cases the first optical density maximum point

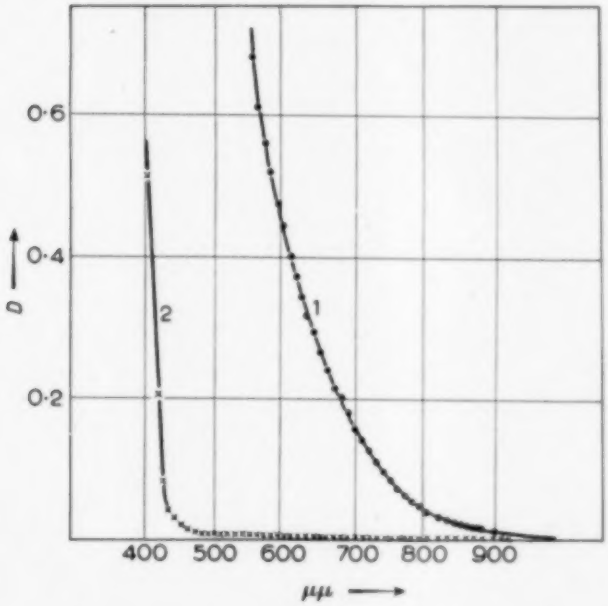


FIG. 2.
1. 3 ml SAO 0·02 M + 2 ml $Co(NO_3)_2$ 0·01 M + 5 ml $H_2BO_3$ 0·2 N + 4·4 ml NaOH 0·2 N + 5·6 ml $H_2O$. pH = 10
2. 3 ml SAO 0·02 M + 5 ml $H_2BO_3$ 0·2N + 4·4 ml NaOH 0·2N + 7·6 ml $H_2O$. pH = 10.

lies at the molar ratio of 2 Co(III) : 3 $SAO^{-2}$. SAO can therefore be titrated with $Co(NO_3)_2$, and vice versa, at these wavelengths. In addition, results are presented of similar density measurements at pH = 10 (Fig. 4), using the method of continuous variations. Here too, the intersection point lies exactly at the ratio of 2 Co(III): 3 $SAO^{-2}$.

From the above results we learn that the complex which is formed at pH = 7 is subject to no further optical density changes at higher pH's, and is apparently the only one which exists.

2. *Nickel salicylaldoximate.* In contrast to cobalt, nickel with SAO-anion gives either a *solution* or a *precipitate*, depending on the pH. The precipitate, which has the composition of $Ni(SAO)_2$, can be used for heterometric determination of nickel (see special report). Fig. 5 shows three pH-heterometric titrations which were made in order to study the pH-conditions under which either a precipitate or a solution is

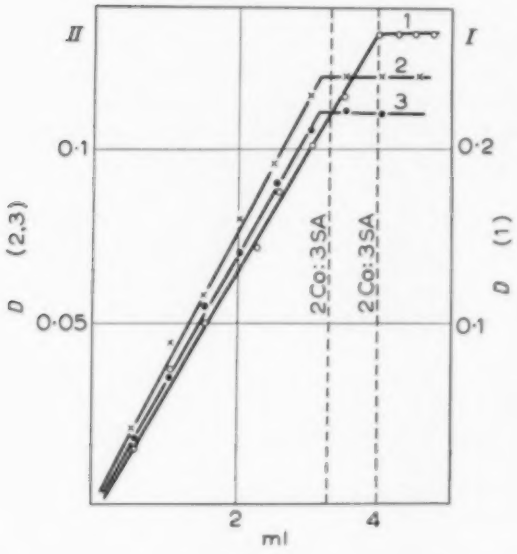


FIG. 3.

1. 5 ml $H_3BO_3$ 0·2 M + 4·4 ml NaOH 0·2 N + 3 ml SAO 0·01 M + $x$ ml $Co(NO_3)_2$ 0·005 M + (7·6 − $x$) ml $H_2O$. $\lambda = 600$ mμ. pH = 10.
2. 5 ml SAO 0·001 M + 5 ml $NH_3$ N + 1 ml $NH_4NO_3$ M + (9 − $x$) ml $H_2O$ + $x$ ml $Co(NO_3)_2$ 0·001 M. $\lambda = 500$ mμ
3. 5 ml SAO 0·0005 M + 5 ml $NH_3$ N + 1 ml $NH_4NO_3$ M + (9 − $x$) ml $H_2O$ + $x$ ml $Co(NO_3)_2$ 0·0005 M. $\lambda = 450$ mμ

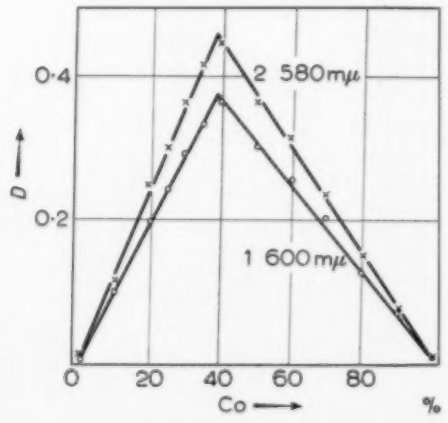


FIG. 4.

$x$ ml $Co(NO_3)_2$ 0·005 M + (10 − $x$) ml SAO 0.005 M + 5 ml $H_3BO_3$ 0·2 M + 4·4 ml NaOH 0·2 N + 0·6 ml $H_2O$. (1) = 600 mμ; (2) = 580 mμ. pH = 10.

obtained. Both $NH_3/NH_4NO_3$ and borate buffer solutions were used. The details of the experiments and the sort of titrations made may be seen from the figure. The pH's which correspond to the titration curves are shown by curves and are designated with "*a*". No filter was used for the heterometric titrations. An analysis of these curves

shows the following: on raising the pH's of the solution (curve 1 and 1a), an abrupt precipitation occurs at pH ~5·7 and the precipitation is quantitative at pH ~6.2. Between pH's 6·2 and 11, the precipitate remains unchanged. At pH = 11 the dissolution begins and is quantitative at pH ~12·5. Curve 2 presents the reverse heterometric titration which begins at a high pH (the abscissa shows the reverse scale). On the addition of nitric acid, the pH's decrease and the precipitation occurs abruptly and is quantitative at pH ~12. No change occurs till the pH decreases to ~5·6, which corresponds to the point of the initial precipitation in curve 1. At lower pH's the precipitate dissolves rather slowly.

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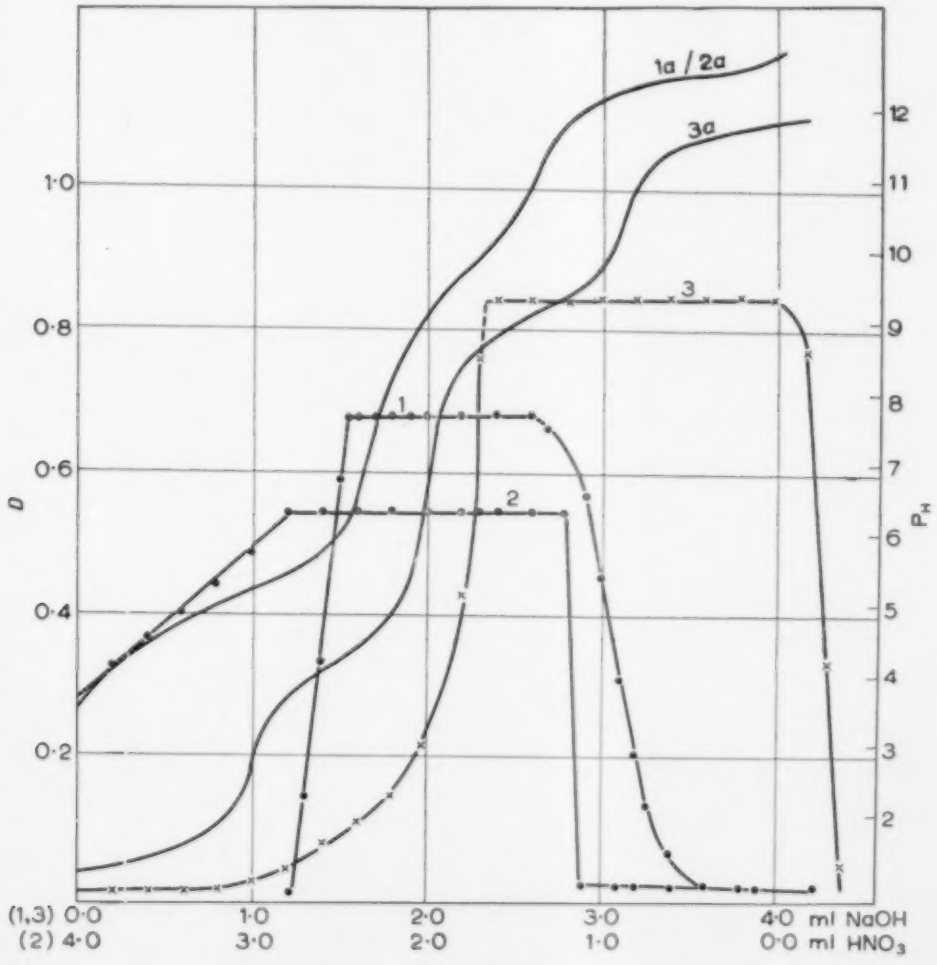



FIG. 5.
1. 3 ml $Ni(NO_3)_2$ 0·005 M + 1·5 ml $CH_3COOH$ 0·4 N + 3 ml $H_3BO_3$ 0·2 N + 2·5 ml SAO 0·02 M + 10 ml $H_2O$ + *x* ml NaOH N.
2. 3 ml $Ni(NO_3)_2$ 0·005 M + 1·5 ml $CH_3COOH$ 0·4 N + 3 ml $H_3BO_3$ 0·2 N + 2·5 ml SAO 0·02 M + 4 ml NaOH 0·4 N + 6 ml $H_2O$ + *x* ml $HNO_3$ 0·4 N.
3. 3ml $Ni(NO_3)_2$ 0·005 M + 1 ml $HNO_3$ N + 1 ml $CH_3COOH$ M + 2 ml $NH_4NO_3$ M + 4 ml SAO 0·01 M + 9 ml $H_2O$ + *x* ml NaOH N. 1a–3a, pH curves.

Summarizing, we may conclude that quantitative precipitation occurs between pH 6–12. On raising the pH further, even by tenth units of pH, the insoluble complex is dissolved abruptly and quantitatively. Curve 3 (and 3a) presents a similar pH-heterometric titration which was carried out in the presence of $NH_3/NH_4NO_3$ buffer solution. The differences in the results obtained at high pH's in the latter case may be

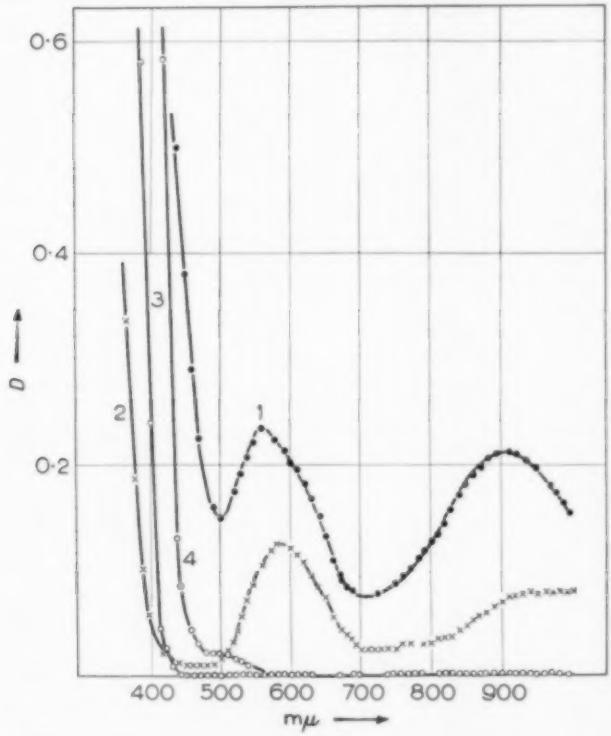



FIG. 6.
1. 2 ml $Ni(NO_3)_2$ 0·1 M + 2 ml $NH_3$ 9 N + 3 ml SAO 0·2 M alc. + 2 ml alc. + 1 ml $H_2O$.
2. 2 ml $Ni(NO_3)_2$ 0·1 M + 2 ml $NH_3$ 9N + 1 ml $H_2O$ + 5 ml alc.
3. 3ml SAO 0·2 M alc. + 2ml alc. + 5ml $H_2O$.
4. 3 ml SAO 0·2 M alc. + 2 ml alc. + 2 ml $NH_3$ 9N + 3 ml $H_2O$.

caused by a loss of ammonia during the titration. Analysing curve 3, we may conclude as follows: complete precipitation occurs with ammonia between pH ~8·6 and ~12. The precipitate redissolves abruptly and quantitatively at pH $\geqslant$ 12, just as in the *absence* of $NH_3$ (curve 2). We may therefore conclude that here, too, *the presence of* $NH_3$ *does not interfere at high* pH's *with the* Ni-SAO *complex* which is formed. The doubts cast upon the character of the complex which is formed in solution at high pH's, are therefore unfounded.[2] On the other hand, $NH_3$ does interfere to some extent in the pH region of 6–9.

The following experiments were made to investigate the character, composition, and stability of the *soluble* nickel complex. Fig. 6 shows the absorption spectra of the *soluble* nickel oximate, the nickel-$NH_3$ complex, both in excess of $NH_3$, and the absorption spectrum of SAO (in the presence and in the absence of $NH_3$). The maximum

absorption of the Ni-SAO complex lies at 560 m$\mu$, whilst in the case of the Ni-$NH_3$ complex this maximum lies at 580 m$\mu$. Between 450 m$\mu$ and 500 m$\mu$ the absorption of the Ni-$NH_3$ complex, as well as SAO-$NH_3$, is very low. On the basis of these spectra, the method of continuous variations was used to investigate the composition and the stability of the *soluble* nickel-SAO complex at high pH. The measurements

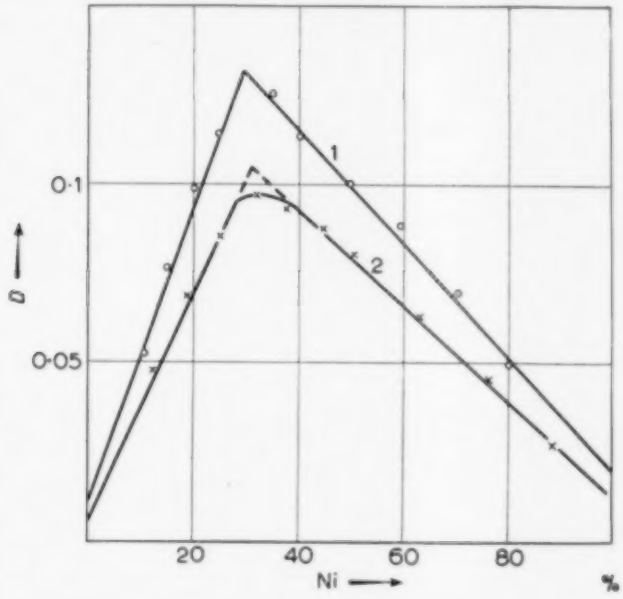



FIG. 7.
1. $x$ ml $Ni(NO_3)_2$ 0·2 M + (10 − $x$) ml SAO 0·2 M + 5 ml $NH_3$ 6N + 5 ml alc. Solution 50% alc. $\lambda$ = 500 m$\mu$.
2. $x$ ml $Ni(NO_3)_2$ 0·2 M + (8 − $x$) ml SAO 0·2M + 5 ml $NH_3$ 6N + 5 ml alc. Solution 50% alc. $\lambda$ = 500 m$\mu$.

were made at 500 m$\mu$. The results are seen in Fig. 7, and show that the composition of the soluble complex is 1 $Ni^{2+}$: 2 $SAO^{-2}$. The calculated mean dissociation constant is given by

$$K = [Me^{2+}][SAO^{-2}]^2/[Me(SAO)_2]$$
$$= 1{\cdot}7 \times 10^{-4}$$

$K$ was calculated assuming that the SAO acts in the high pH region as $SAO^{-2}$ only.

3. *Copper salicylaldoximate*. A study of the copper oximate has been carried out by us in connection with the heterometric determination of copper, the results of which are presented elsewhere[4] In that study, pH-heterometric curves were presented, and it was found that the *insoluble* $Cu(SAO)_2$ is formed quantitatively in the pH region of 3–10. Between pH's 10–11 the insoluble compound is dissolved quantitatively. The *soluble* copper salicylaldoximate is stable at pH $\geqslant$ 11. The *soluble* complex was investigated by us spectrophotometrically. Fig. 8 shows the different spectra as well as the composition of the experiments. A comparison of the curves 2, 4, and 5 shows that in all three cases the optical maximum density lies at the wavelengths of 580–590

[4] M. BOBTELSKY and E. JUNGREIS *Anal. Chim. Acta* **13**, 449 (1955)

mμ. Identical absorption spectra are obtained both in the presence of $NH_3$ and in the presence of borate solutions. The curves 4 and 5 show high absorption at wavelengths <500 mμ which is caused by the influence of the SAO-*liquid*. This is in contrast to the Cu-$NH_3$ complex, which does not absorb at 400–500 mμ. *The ammonia therefore does not in any way interfere with the spectrum of copper salicylaldoximate at high* pH's. *This latter is the only complex which is formed at high* pH's *in the* SAO-*solutions*. The doubt about the character of this complex[2] may therefore be considered as settled.

In all the copper complexes the maximum is shifted to the lower wavelengths by

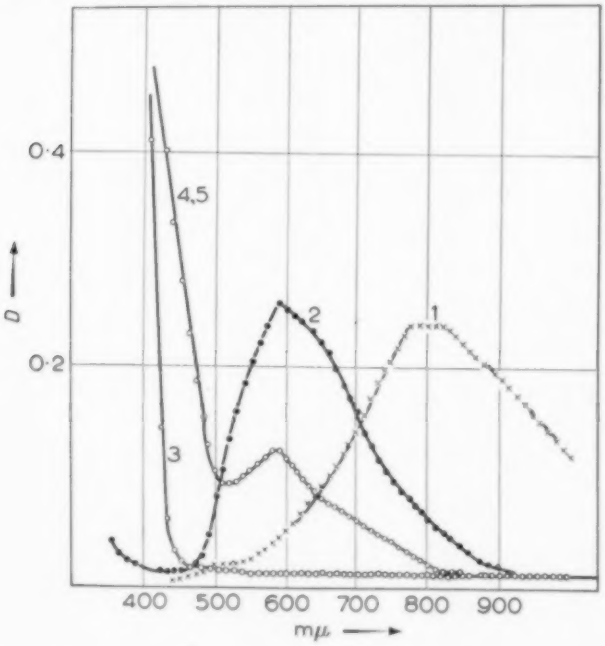



FIG. 8.

1. 2 ml $CuSO_4$ 0·1 M + 8 ml $H_2O$.
2. 1 ml $CuSO_4$ 0·1 M + 5 ml $NH_3$ 2N + 14 ml $H_2O$.
3. 5 ml SAO 0·02 M + 5 ml $NH_3$ 2N + 10 ml $H_2O$.
4. 3 ml SAO 0·02 M + 6 ml $H_3BO_3$ 0·2 N + 3 ml NaOH 0·2 N + 2 ml $CuSO_4$ 0·01 M + 6 ml $H_2O$.
5. 3 ml SAO 0·02 M + 5 ml $NH_3$ 2N + 2 ml $CuSO_4$ 0.01 M + 10 ml $H_2O$.

about 200 mμ in comparison with the spectrum of the solvated copper ion (curve 1). From the curves it may be deduced that the molar absorption at high pH of the soluble complex $[Cu(SAO)_2]^{2-}$ is at 580–590 mμ—about 2·5 times higher than that of the $[Cu(NH_3)_4]^{2+}$ complex. On the basis of these curves, Job measurements were carried out at 460 mμ. The composition of the experiments and the results obtained are shown in Fig. 9. As we see, the composition of the soluble copper complex is $[Cu(SAO)_2]^{2-}$. Calculations of the dissociation constants (similar to those of nickel) gave a mean value of $K_{Cu} = 6{\cdot}4 \times 10^{-5}$.

## DISCUSSION

The existence of the following *soluble* complexes was established: $[Co_2(SAO)_3]^0$, $[Ni(SAO)_2]^{2-}$ and $[Cu(SAO)_2]^{2-}$. In contrast to the last two, the cobalt complex is

already formed quantitatively at pH = 7–8, and remains unchanged at high pH's. Once formed, it is apparently stable at lower pH's. The spectrum of cobalt shows no maximum in the region of 500 m$\mu$ and is therefore *different* from the spectrum of cobalt(II) citrate or other cobaltous complexes. The optical sensitivity is very high, and the complex is formed quantitatively from the components, even if present in very low concentrations. All this signifies that the cobalt is present in the trivalent form. Entirely different is the behaviour of the nickel and copper complexes. Both the insoluble as well as the soluble SAO-compounds have the stoichiometric composition

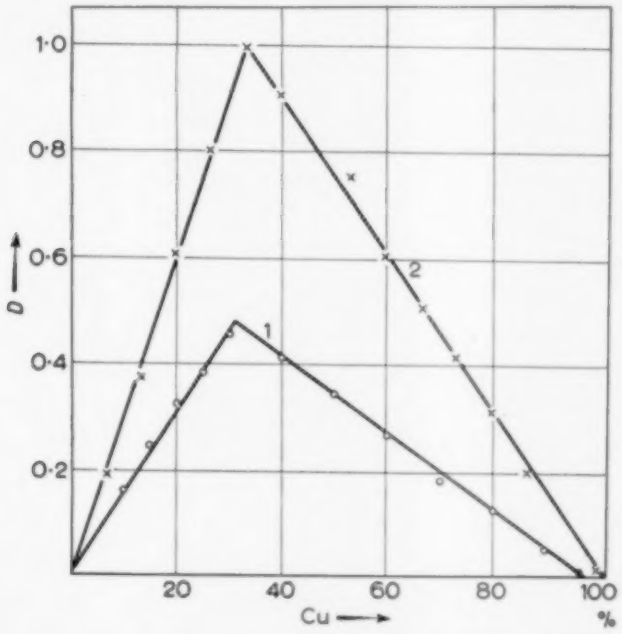


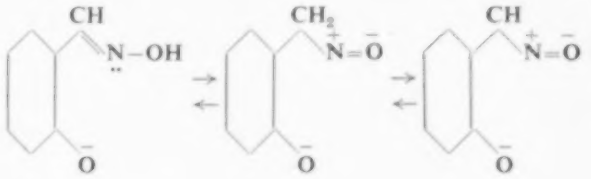

FIG. 9.
1. $x$ ml $CuSO_4$ 0·01 M + (10 − $x$) ml SAO 0·01 M + 5 ml $NH_3$ 2N + 5 ml $H_2O$
2. $x$ ml $CuSO_4$ 0·01 M + (15 − $x$) ml SAO 0·01 M + 5 ml $NH_3$ 2N
$\lambda = 460$

of 1 $Me^{2+}$: 2 $SAO^{-2}$. The *insoluble* nickel-SAO compound begins to precipitate at pH ~5·7 and is quantitative at pH ~6·2. It exists without alteration between the pH's of 6–12. The insoluble copper-SAO compound is already formed quantitatively at pH ~3, and exists without alteration in the pH region of 3–10. At pH ⩾12 the insoluble nickel compound is transformed quantitatively and abruptly into a *soluble* complex, whilst the corresponding soluble copper complex is formed abruptly at pH ⩾11. The stability of both *soluble* complexes ($K_{Ni} = 1{\cdot}7 \times 10^{-4}$ and $K_{Cu} = 6{\cdot}4 \times 10^{-5}$) is not very different. Both are probably more electrostatic complexes (just as are the corresponding citrates).

It is reasonable to assume that in the *insoluble* salicylaldoximates of Ni and Cu, the structure of the SAO is different from the SAO radical which participate in the formation of the soluble complexes at pH's 11–12. How far a rearrangement of SAO-radical takes place is not easy to tell with certainty. Probably both the electronic

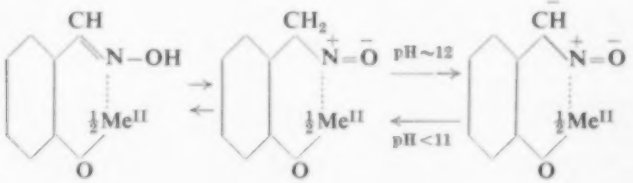
and the steric moments are involved. In any case, we may assume that in the acid and the neutral pH-regions, SAO acts in some "*a*" form, while at very high pH's a "*b*" form must exist. In the "*a*" form one proton is substituted by the cation. In the "*b*" form a possibility exists that *another* proton may be neutralized at the very high pH's, just as is the case with many oxy-compounds (citrates, tartrates, etc.). In any case, the abrupt quantitative dissolution of the insoluble nickel and the copper complexes in a very narrow pH region is most significant.

We may now attempt to present the SAO structures which exist at the different conditions. They may be presented as follows:



(1) (2) (3)

The insoluble compounds which are formed with the metals at lower pH's may have the structure (4) or (5):




(4) (5) (6)

The soluble complexes which are obtained at the high pH's may be constructed as (6), giving the anion complex $[Me^{II}(SAO)_2]^{2-}$. Nothing can be said with certainty as to which of the two structures (4) or (5) does participate at lower pH's in each case.

Another possibility of course would be that both the soluble and the insoluble compounds form *neutral* molecules, which differ only in the tautomeric forms of SAO which participate in their formation.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 49 to 53. Pergamon Press Ltd., London

# ANION-EXCHANGE SEPARATION OF MOLYBDENUM AND TECHNETIUM AND OF TUNGSTEN AND RHENIUM

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(*Received 5 April* 1956)

**Abstract**—The present work was designed to meet a need in radiochemistry for the ready separation of molybdenum and technetium and of tungsten and rhenium. The distribution coefficients for these elements on an anion-exchange resin have been determined in hydrochloric- and nitric-acid solutions of varying concentration. These values were used to determine suitable conditions for separating these elements and recovering them in small volumes free of material which would interfere in measuring their activities.

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THERE is a need in radiochemistry for suitable separations of molybdenum and technetium and of tungsten and rhenium. Such a need may occur in bombardments of molybdenum and tungsten targets and in the separation of some mother-daughter pairs. The solutions containing the separated elements should allow ready evaporation on counting plates and should not contain appreciable amounts of substances which would absorb the radiation or cause loss of activity on being decomposed or fumed. For these reasons such materials as sodium hydroxide, organic acids, salts, perchloric acid, and sulphuric acid should be avoided. The separations should be reasonably fast and should not require large volumes of solution. Anion-exchange methods using only the readily volatile hydrochloric and nitric acids appeared to offer favourable conditions for these separations, and the present paper reports the results of studies on these systems.

The separation of molybdenum and rhenium by anion exchange, including hydrochloric acid eluants, has been studied by FISHER and MELOCHE[1] and by MELOCHE and PREUSS.[2] These separations used sodium hydroxide, potassium oxalate, and perchloric-acid eluants in parts of their schemes. The first two materials cannot be evaporated from a counting plate, and the last causes loss of activity when it is fumed. Column elutions of molybdenum and tungsten with hydrochloric acid, the latter in a limited range of acid concentration, have been made by KRAUS, NELSON, and MOORE,[3] and a qualitative statement regarding the behaviour of technetium has been made by these authors.

## EXPERIMENTAL

*Materials and analyses.* Dowex-1 in the chloride form, 250–500 mesh, dried over magnesium perchlorate, and all from one lot, was used for both the batch equilibrations and the column separations in hydrochloric acid. For the batch equilibrations in nitric acid the resin was treated in a column with 2 M nitric acid until a negative test for chloride was obtained in the eluant. The resin was then washed with water and dried over magnesium perchlorate.

Reagent-grade sodium molybdate dihydrate (Baker and Adamson) was used as the source of

[1] S. A. FISHER and V. W. MELOCHE *Analyt. Chem.* **24**, 1100 (1952).
[2] V. W. MELOCHE and A. F. PREUSS *Analyt. Chem.* **26**, 1911 (1954).
[3] K. A. KRAUS, F. NELSON, and G. E. MOORE *J. Amer. Chem. Soc.* **77**, 3972 (1955).



4 (20 pp.)

molybdenum. The polarographic method of STACKELBERG *et al.*, as given by KOLTHOFF and LINGANE,[4] was used to analyse the molybdenum content of the solutions in determining the distribution coefficients, but the spectrophotometric method given by SANDELL[5] was used during the column separation from technetium because of the much lower concentrations in some samples. One-tenth of the quantities recommended in the latter method were used, keeping the concentrations the same. Readings were taken with a Beckman Model DU spectrophotometer.

Fission-product $Tc^{99}$ was obtained from the Oak Ridge National Laboratory in the form of potassium pertechnetate having a specific activity of about 20 microcuries per milligram of technetium. All analyses were made by evaporating suitable aliquots on platinum plates and counting in a G-M counter.

The tracer $W^{185}$, prepared by pile irradiation of tungsten, was obtained from the Oak Ridge National Laboratory as a solution of potassium tungstate. A tenfold dilution of this solution in 0·9 M hydrochloric acid was used as a stock solution. Analyses were made by counting dried aliquots on platinum discs.

Potassium perrhenate was obtained from A. D. MELEVAN, University of Tennessee. This material, 99·9% pure, as indicated by spectrographic analysis, was used in determining the distribution coefficients of rhenium in hydrochloric acid. Aliquots for analysis containing 25–100 micrograms of rhenium were evaporated to dryness, taken up in one millilitre of 4·0 M perchloric acid and run on a polarograph. Preliminary studies had shown this analysis to be reliable and not critically dependent on the concentration of perchloric acid. A mixture of the tracers $Re^{183}$ and $Re^{184}$ was used for the determination of the distribution coefficients in nitric acid and for the column separation for tungsten. This material, obtained from J. O. RASMUSSEN of this laboratory, had been prepared by an alpha-particle bombardment of tantalum in the 60-inch cyclotron and was electroplated on a platinum-wire cathode. It was dissolved from the wire in a few drops of concentrated nitric acid, heated to near dryness to oxidize to perrhenic acid and taken up in 1·0 M hydrochloric acid, or in 1·0 M nitric acid for the equilibrations in nitric acid. Analyses were made by counting suitable aliquots evaporated on platinum discs.

*Distribution coefficients.* Between 2 and 50 mg of resin were mixed with 2–50 ml of solution for at least 15 hours at 25°, though equilibrium was apparently attained in not over two hours for all four elements. These weights and volumes were chosen so that the distribution between resin and solution was approximately equal, in order to obtain maximum accuracy in the determination of the coefficient. This sometimes required preliminary trials to find approximate values. The solutions were prepared by adding aliquots of stock solutions to measured volumes of hydrochloric or nitric acid of known concentration. The final acid concentration was generally determined from these dilutions but was sometimes checked by an analysis of the solution after equilibration with resin. In no case was the foreign-ion concentration, such as that of sodium from the sodium molybdate, over 0·001 molar. Aliquots of solution were analysed after equilibration, and the amount of element adsorbed on the resin was determined by difference.

*Separations.* The optimum concentrations of hydrochloric acid for the separations were chosen from the results found for the distribution coefficients. Molybdenum and technetium in 0·5 ml of 1·0 M hydrochloric acid were added to a column of resin 3 mm in diameter and 21 mm in length. When the levels of liquid had just reached the top of the resin, elution was continued with 1·0 M hydrochloric acid, at the rate of 1 ml in 15 minutes, to remove molybdenum. Technetium was then removed from the column with 4·0 M nitric acid at the same rate of elution. Similarly, tungsten and rhenium in 1 ml of 1·5 M hydrochloric acid were added to a column 4 mm in diameter and 50 mm in length and the tungsten was eluted with the same acid. Rhenium was then eluted with 4·0 M nitric acid.

## RESULTS

The distribution coefficient is defined by the equation:

$$K_D = \frac{M_r \text{ x ml solution}}{M_l \text{ x g resin}}$$

[4] I. M. KOLTHOFF and J. J. LINGANE *Polarography*, 2nd ed. Interscience Publishers, New York and London, p. 613 (1952).

[5] E. B. SANDELL *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York, p. 333 (1944).

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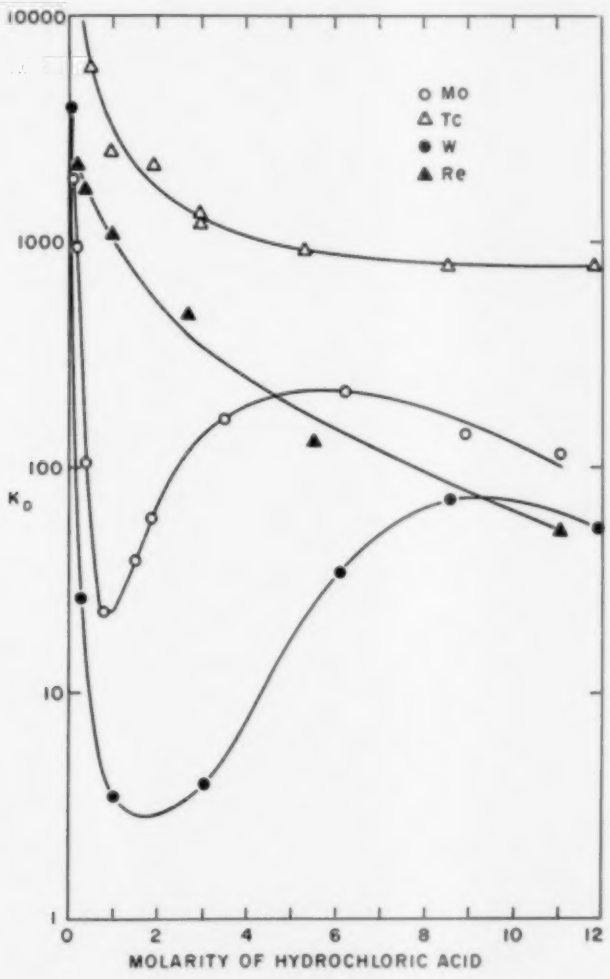


FIG. 1.—Dependence of the distribution coefficient at 25° on the hydrochloric-acid concentration with Dowex-1.

where $M_r$ and $M_l$ are the fractions of the measured element in the resin and liquid phases, respectively. The dependence of $K_D$ on the concentration of hydrochloric acid for the four elements is shown in Fig. 1, and the dependence on the concentration of nitric acid, for technetium and rhenium, is shown in Fig. 2. The curves for molybdenum and rhenium in hydrochloric acid are similar to those of MELOCHE and PREUSS,[2] who used Amberlite IRA-400 instead of Dowex-1, but the $K_D$ values

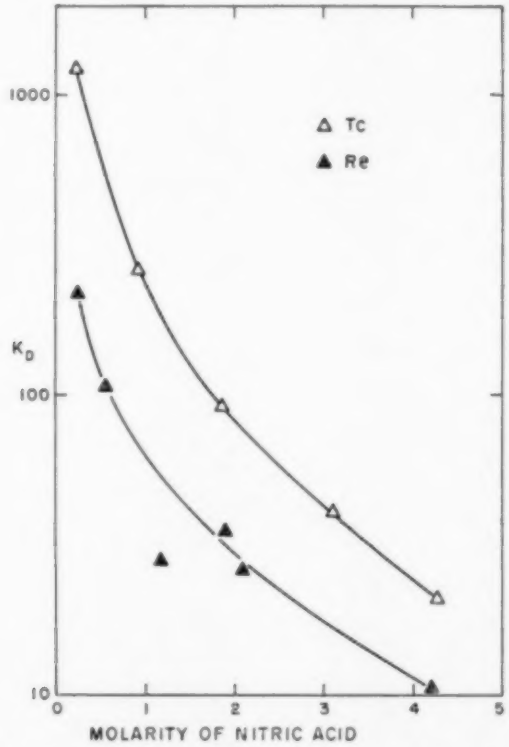


FIG. 2.—Dependence of the distribution coefficient at 25° on the nitric-acid concentration with Dowex-1.

are about double their values. The present results indicate that the best separation of molybdenum and technetium should occur in about 1 M hydrochloric acid and the best separation of tungsten and rhenium in about 1·5 M hydrochloric acid.

Fig. 3 gives the results of separating molybdenum and technetium in about the optimum concentration of hydrochloric acid, followed by the elution of technetium in 4·0 M nitric acid. The total molybdenum recovered in the first 4·0 ml of hydrochloric acid was 100% of the amount used and the recovery of technetium in the first 4·4 ml of nitric acid was 98%. For some reason, 0·1% of the technetium activity appeared in the first millilitre of hydrochloric acid with the molybdenum, but no more appeared in the next 7 ml. To investigate the possibility that a foreign activity gave this result the technetium was recovered from the nitric-acid eluant, and the separation was repeated. Again, 0·1% of the technetium activity appeared in the first millilitre of hydrochloric acid; any impurity should have been removed in the first run.

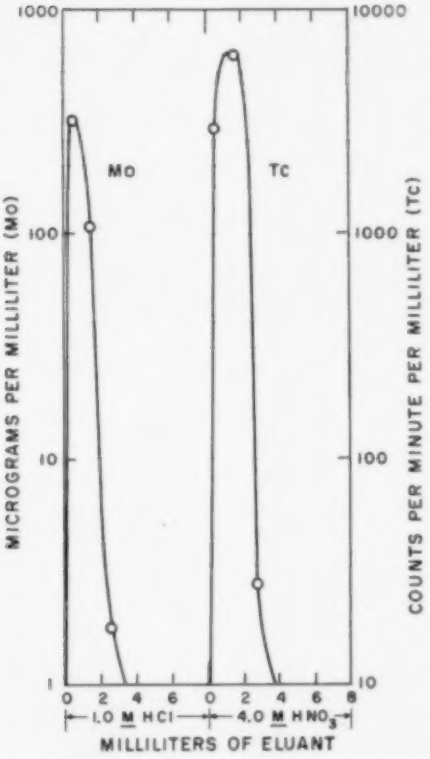


FIG. 3.—Separation of molybdenum and technetium on Dowex-1; column 3 mm × 21 mm.

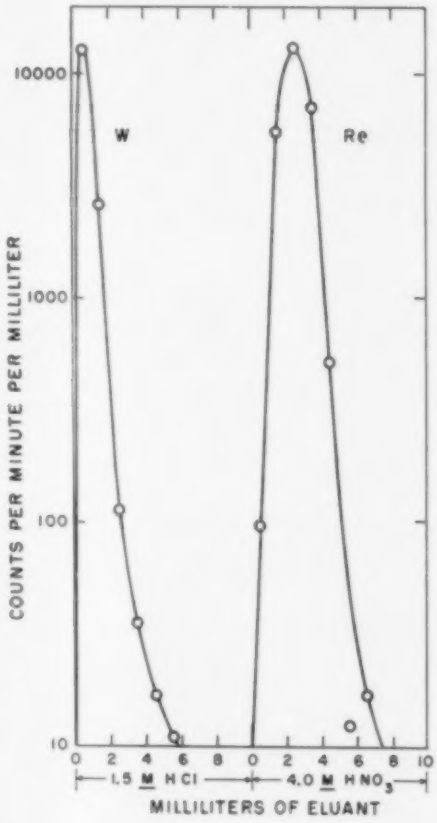


FIG. 4.—Separation of tungsten and rhenium on Dowex-1; column 4 mm × 50 mm.

The results of separating tungsten and rhenium are shown in Fig. 4. A recovery of 101% of the tungsten was found in the first 6·0 ml of 1·5 M hydrochloric acid and a recovery of 93% of the rhenium was found in the first 8 ml of 4·0 M nitric acid. A longer column was used for this separation than for molybdenum and technetium because of the lower $K_D$ values for this pair of elements.

The distribution coefficients previously obtained in perchloric acid for rhenium[2] indicate that this eluant would be better than nitric acid for the recovery of rhenium, and probably for technetium. When attempts were made to fume perchloric acid from counting plates, however, about half of the rhenium or technetium activity was lost. A readily volatile eluant is needed for easy recovery.

*Acknowledgement*—This work was done under the auspices of the U.S. Atomic Energy Commission.

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J. Inorg. Nucl. Chem., 1956. Vol. 3, pp. 54 to 63. Pergamon Press Ltd., London

# THE SEPARATION OF PLUTONIUM BY EXTRACTION WITH THENOYLTRIFLUORACETONE (TTA)

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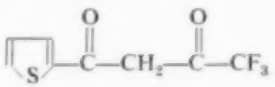
(*Received* 21 *March* 1956)

**Abstract**—This paper discusses the separation of plutonium by solvent extraction with TTA solutions. Distribution ratio data are presented together with an experimental survey of the factors affecting them. Values have been calculated for the equilibrium constant of the solvent extraction reaction for tetravalent plutonium.

## 1. INTRODUCTION

### (a) *TTA as a Chelating Agent*

2-THENOYLTRIFLUOROACETONE (usually abbreviated to TTA) was first prepared by REID and CALVIN,[1] and has the formula



when in the keto form. It is a solid at ordinary temperatures (m.p. 42·5–43·2°C) and it is relatively insoluble in water, but is easily soluble in a large number of organic solvents, such as benzene, carbon tetrachloride, etc. This solubility is shared by the metal chelates. It is a strong complexing agent for many metal ions in acid solution, particularly for those of higher valency.

It has been used as a chelating agent by many workers,[2–7] and the first published reference to its use in a process for the large-scale separation of plutonium from uranium was given in a recent paper by CULLER.[8]

If the slight solubility of TTA in the aqueous phase and of the aqueous substrate in the organic phase are ignored, the reaction to form the metal chelate may be written as

$$\underset{\text{aqueous}}{M_n^+} + n\underset{\text{solvent}}{HT} \rightleftharpoons \underset{\text{solvent}}{MT_n} + n\underset{\text{aqueous}}{H^+}$$

and the equilibrium constant for extraction of a metal into an organic solution containing TTA is then

$$C = \frac{\{MT_n\}_{org}\{H^+\}^n_{aq}}{\{M^{n+}\}_{aq}\{HT\}^n_{org}} \qquad (1)$$

where the brackets denote activities.

* Australian Atomic Energy Commission.

[1] J. C. REID and M. CALVIN *U.S.A.E.C. Declassified Document MDDC* 1405 (1947).
[2] R. A. BOLOMEY and L. WISH *J. Amer. Chem. Soc.* **72**, 4483 (1950).
[3] J. P. MCBRIDE *U.S.A.E.C. Unclassified Document A.E.C.U.* 399 (1949).
[4] E. H. HUFFMAN and L. J. BEAUFAIT *J. Amer. Chem. Soc.* **71**, 3179 (1949). R. E. CONNICK and W. H. MCVEY *J. Amer. Chem. Soc.* **71**, 3182 (1949).
[5] G. N. WALTON, F. BARKER, G. BYFLEET; *U.K.A.E.A. Unclassified Report A.E.R.E. C/R* 768 (1951).
[6] J. G. CUNINGHAME, P. SCARGILL, and H. H. WILLIS *U.K.A.E.A. Unclassified Report A.E.R.E. C/M* 215 (1954).
[7] E. H. COOK and R. W. TAFT *J. Amer. Chem. Soc.* **74**, 6103 (1952).
[8] F. L. CULLER Paper P/822 presented at the Geneva Conference on the Peaceful Uses of Atomic Energy 1955.

The full expression for the equilibrium constant, for the case of the extraction of tetravalent plutonium in nitric acid, is given by

$$C' = \frac{[PuT_4]_{org}\, f_{PuT_4}\, [HNO_3]^8\, y^8_{\pm HNO_3}}{\alpha[Pu]_{aq}\, [NO_3^-]^4\, y^5_{\pm Pu(NO_3)_4}\, [HT]^4\, f^4_{HT}}$$

$$= K_{Pu} \times \frac{f_{PuT_4}}{[HT]^4 f^4_{HT}} \times \frac{a^4_{HNO_3}}{\alpha y^5_{\pm Pu(NO_3)_4}\, [NO_3^-]^4} \qquad (2)$$

where the bracketed species represent concentrations, $y$'s represent aqueous-phase activity coefficients, and $f$'s activity corrections for the un-ionized species in the organic phase. $K_{Pu}$ is the distribution ratio, $[PuT_4]_{org}/[Pu]_{aq}$, $\alpha$ is the fraction of uncomplexed plutonium in the aqueous phase, and $a_{HNO_3}$ the activity of nitric acid.

The sensitivity of the equilibrium to acid concentration (particularly for high-valence ions), the strong chelating power of the reagent, and its stability in strongly acid solutions, make the reagent very suitable for the separation of plutonium, which can readily be obtained in the tetravalent state.

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(b) *Conditions for Optimum Plutonium Extraction*

The equilibrium constants $C$ (equation 1 above) for benzene/TTA solutions and plutonium in various valency states are as follows:

| | |
|---|---|
| $Pu^{3+}$ | $\sim 3$ (see para. 4) |
| $Pu^{4+}$ | $\sim 10^5$ (see para. 5) |
| $PuO_2^+$ | low |
| $PuO_2^{2+}$ | low (probably about $10^{-1}$–$10^{-2}$ by analogy with $UO_2^{2+}$). |

The most important equilibrium for plutonium in acid solution is probably represented by the equation

$$3Pu^{4+} + 2H_2O \rightleftharpoons 2Pu^{3+} + PuO_2^{2+} + 4H^+ \qquad (3)$$

while a second equilibrium is represented by

$$Pu^{4+} + PuO_2^+ \rightleftharpoons PuO_2^{2+} + Pu^{3+} \qquad (4)$$

The latter equilibrium is established rapidly in solution, since the breaking of oxygen bonds is not involved in it, but only the transfer of an electron. The equilibrium given in equation (3), however, is a higher-order reaction (the rate-controlling step is probably bimolecular) and is established slowly. The rate of disproportionation of tetravalent plutonium in nitric acid has been studied by G. R. HALL.[9] He found that for a Pu(IV) solution with a concentration of 2 mg Pu/ml in 0·344 M nitric acid, equilibrium was reached in approxiamtely 17 hours, at which time the solution contained 12% Pu(III), 66% Pu(IV), and 22% Pu(VI). This disproportionation will also depend on plutonium concentration. A full discussion of the equilibria is given in reference (10).

It can thus be seen that it is necessary to prepare the plutonium in the tetravalent state prior to extraction and to carry out the extraction before disproportionation has had time to occur.

[9] G. R. HALL Unpublished work at A.E.R.E. Harwell (1952).
[10] R. E. CONNICK *The Actinide Elements* N.N.E.S. IV—14A.

(c) *Preparation of Tetravalent Plutonium Solutions*

The redox potential of the system Pu(VI)—Pu(IV) in 1 M nitric acid at 25–30°C is approximately −0·76 V referred to the 1 M calomel electrode, and that of the Pu(IV)—Pu(III) system is about −0·64 V.[11] BUNCE and NYE[12] found for 0·5 M

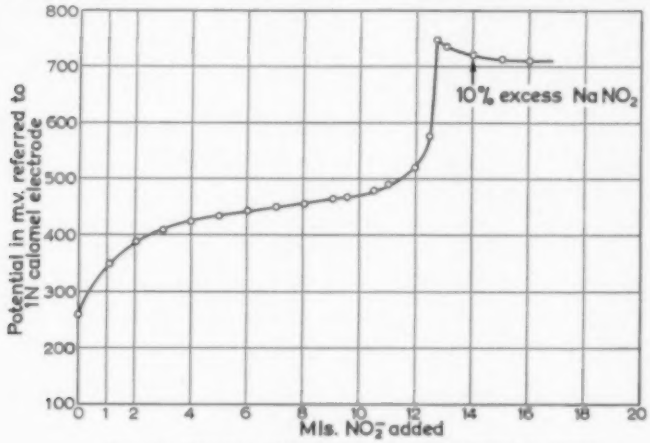


FIG. 1.—Titration of $NaNO_2$ against $N_2H_4HNO_3$ in $HNO_3$.

nitric acid a value of −0·646 V for the Pu(IV)—Pu(III) system referred to the 1 M calomel electrode, and this was apparently little changed by the presence of ammonium nitrate.

A suitable method of preparing tetravalent plutonium is by the reduction of all the plutonium to the trivalent state with a reducing agent such as hydrazine, followed by oxidation with nitrite. Fig. 1 shows the observed potentials when a 0·1 M solution of sodium nitrite was titrated against

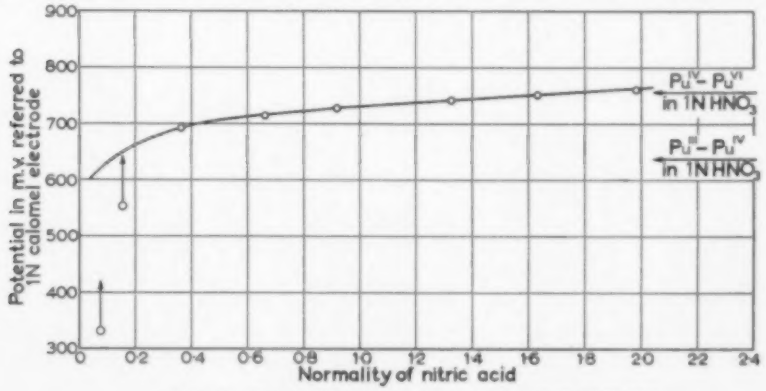


FIG. 2.—Potential of nitric acid containing 0·01 M $NaNO_2$.

a 0·1 M solution of hydrazine nitrate in nitric acid at 21°C. At the neutralization point, the system is, to a first approximation, merely nitric acid, and should show the potential appropriate to that acidity; this potential will probably be only reproducible to about 25 mV, but it should be possible to predict to this accuracy the final potential which will be obtained at any acidity, from a graph of nitric acid concentration against potential. Such a graph is shown in Fig. 2; the nitric acid contains nitrite

[11] E. L. KING and W. H. REAS *J. Amer. Chem. Soc.* **73**, 1804 and 1806 (1951).
[12] J. L. BUNCE and J. D. NYE Unpublished work at A.E.R.E. Harwell (1950).

at 0·01 M, corresponding to a 10% excess of nitrite over hydrazine. It is worth noting that the potential found for 1 M nitric acid (0·735 V referred to 1 M calomel electrode) agrees well with the potential at 10% past the end point of the nitrite-hydrazine titration in 1 M acid (−0·725 V) of Fig. 1. The addition of excess nitrite causes the potential to fall off quite slowly and a 25% excess of it should have little effect on the proportion of Pu(IV) in the system.

From a consideration of the potentials given above, it will be seen that in 1 M nitric acid solution containing excess nitrite, the ratio of Pu(IV) to Pu(III) at equilibrium should be about 40.

## 2. SELECTION OF A SOLVENT FOR TTA

### (a) *Solubility of Thorium-, Zirconium-, and Plutonium-TTA Complexes*

Benzene is the diluent which has been most frequently used in solvent extraction experiments employing TTA, but a wide variety of other organic solvents are suitable. In the early stages of this work it was decided to investigate the possibilities of using a non-inflammable solvent as an alternative to benzene.

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In the early stages of the work, before large quantities of plutonium became available, experiments were made with thorium and zirconium as substitutes for plutonium, in order to gain some idea of the possible behaviour of the plutonium chelate at higher concentrations. The TTA complexes of thorium and zirconium were prepared in solid form from solutions which contained $Th^{234}$ or $Zr^{95}$ respectively, and solubility experiments were carried out with a wide range of solvents. It was found that the results were extremely variable and did not represent the behaviour of the plutonium chelate, when sufficient plutonium became available to use it in similar experiments. A direct determination of the solubility of the plutonium-TTA complex in a 0·5 M TTA-benzene solution was made as follows:

An aqueous solution 0·5 M in nitric acid, and containing 4 mg/ml of plutonium, was extracted with a half volume of 0·5 M TTA in benzene. A brown crystalline precipitate appeared, the benzene was allowed to stand at 20°C, and samples of the supernatant solution were analysed after 48 hours and 96 hours. From the $\alpha$ activity of the solutions the solubility of the plutonium chelate was estimated as 2·99 mg Pu/ml after 48 hours and 3·05 mg Pu/ml after 96 hours.

### (b) *Comparison of Plutonium Distribution Ratios (Tracer Studies)*

A comparison of a series of different solvents is given in Table 1. This table includes results which were obtained with two different preparations of plutonium. All extractions were made from 1 M nitric acid, but in one set of extractions the solvents were made 0·2 M in TTA while in the other set

TABLE 1.—COMPARISON OF VARIOUS SOLVENTS FOR TTA USING TRACER PLUTONIUM

| Solvent | Values of $K_{Pu}$ (i.e. distribution ratio) | | | | |
|---|---|---|---|---|---|
| | 0·2 M TTA series | | | 0·5 M TTA series | |
| | Extraction | 1st strip | 2nd strip | Extraction | 1st strip |
| $C_6H_6$ | — | — | — | 11·8 | 96 |
| $CCl_4$ | 8·7 | 28 | 65 | — | 128 |
| $CHCl_3$ | — | — | — | 5·5 | 69 |
| $C_2H_2Cl_4$ | 1·5 | 1·9 | 7 | 40·5 | 245 |
| $C_6H_5Cl_3$ | 7·7 | 41 | 83 | 2·7 | 138 |
| $C_2HCl_3$ | 11·4 | 64 | 92 | 4·4 | 128 |

they were 0·5 M in TTA. In addition, stripping experiments were carried out in which the organic phase containing the extracted plutonium was mixed with an equal volume of fresh nitric acid of the same concentration.

In these, and in other distribution ratio experiments (except where otherwise stated) the two phases were stirred together for 30 min for measurements of extractions into the organic phase and 15 min for stripping of the organic solvent.

All the measurements described in this paper were made at room temperature—approximately 20°C. Normally, equal volumes of organic and aqueous phases were used.

It is probable that the anomalous results obtained with tetrachloroethane in the extractions with 0·2 M TTA solution may be ascribed to decomposition of the solvent, as the TTA solution was not freshly prepared. Preliminary tests with redistilled solvents, with and without dissolved TTA, indicated that tetrachloroethane was one of the less-stable solvents in this series.

It was difficult to see any trends in the comparative experiments. Further work was restricted to benzene (the conventional solvent for TTA) and to carbon tetrachloride. Carbon tetrachloride has the advantages that it is relatively stable, easily available in a pure state, has little solubility in water and is noninflammable. It was found that at room temperature a given weight dissolves an almost exactly equal weight of TTA.

## 3. PARTITION DATA FOR PLUTONIUM-TTA EXTRACTIONS

### (a) *Varying Time of Mixing*

The dependence of the observed distribution ratio for plutonium on the time of mixing was first investigated using tetravalent plutonium solutions prepared by reduction with cold hydroxylamine hydrochloride for half an hour, followed by the addition of a 50% excess of sodium nitrite, after which the solutions were allowed to stand for half an hour before extraction.

A preliminary experiment showed that the distribution ratio was not greatly affected by the amount of agitation. Two portions of a tetravalent plutonium solution in 1 M nitric acid were shaken with a 0·2 M TTA solution in carbon tetrachloride, as follows:—

*A*. 3 min shaking, then 24 min standing in contact, then 3 min shaking.
*B*. 30 min shaking.

The observed distribution ratios were

*A*. $K_{Pu} = 152$
*B*. $K_{Pu} = 198$

These results were not significantly different, because of the possible error in the determination of the low concentration of residual plutonium. Experiments by WALTON[12] with slow and fast stirring of benzene-TTA solutions also showed that the rate of extraction of the plutonium was not greatly dependent upon the stirring rate.

Fig. 3 illustrates the results of experiments designed to check the dependence of the plutonium distribution ratios upon the time of mixing of the phases. Extractions were made with 0·2 M TTA in carbon tetrachloride from 0·5 M nitric acid. The plutonium solution used in run I was different from that used in runs II and III. Runs II and III were designed to test the effect on the extraction of using extra-pure solvent and excluding air from the system. In run II, ordinary A.R. carbon tetrachloride was used, and no attempt was made to exclude air from the system. In run III the carbon tetrachloride was washed with alkali and then water, redistilled twice before use, and the two phases were shaken together in an atmosphere of nitrogen. It will be seen from the graphs that there is

[12] G. N. WALTON Unpublished work at A.E.R.E. Harwell (1950).

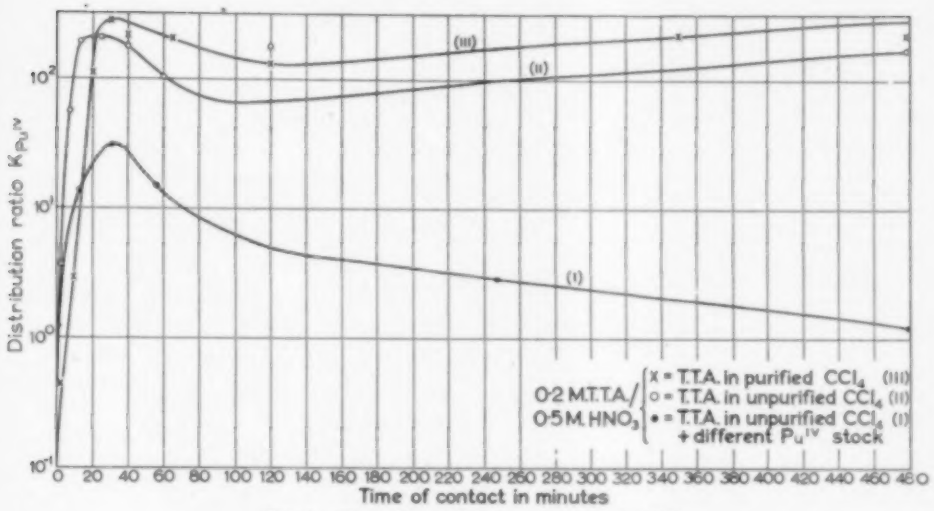
Distribution ratio $K_{Pu^{IV}}$
$10^2$
$10^1$
$10^0$
$10^{-1}$
0 20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480
Time of contact in minutes
(III)
(II)
(I)
0·2 M T.T.A./0·5 M $HNO_3$
x = T.T.A. in purified $CCl_4$ (III)
o = T.T.A. in unpurified $CCl_4$ (II)
• = T.T.A. in unpurified $CCl_4$ (I)
+ different $Pu^{IV}$ stock

FIG. 3.—Dependence of $K_{Pu}$ on time of extraction.

evidence of a maximum in plutonium distribution ratios after about 30 min. It was on the basis of these results that 30 min was selected as a convenient standard time for carrying out the TTA extractions.

(b) *Varying Concentration of TTA*

The effect of varying the concentration of TTA in the system Pu(IV) (trace concentrations)—1 M nitric acid—TTA in carbon tetrachloride is shown in Table 2.

The experiment was conducted as follows: A solution containing a high proportion of tetravalent plutonium was prepared by hydroxylamine reduction and nitrite oxidation and shaken in a flask with carbon tetrachloride, to which regular additions of weighed amounts of TTA were made. The solutions were shaken for 30 min after each addition, and then both phases were sampled.

TABLE 2.—EFFECT OF VARYING THE TTA CONCENTRATION IN THE SYSTEM (TRACE) Pu(IV)—1 N $HNO_3$—TTA IN $CCl_4$

| Concn. of TTA | Distribution ratios org/aq $K_{Pu}$ | Activity coeff. of TTA *KING and REAS[11] $f_{HT}$ | Estimated "effective" TTA activity $f_{HT}/\sqrt[4]{f_{Pu^{IV}}}$ * (cf. equation 2) |
|---|---|---|---|
| 0·02 M | 0·063 | 0·985 | 1·00 (assumed) |
| 0·05 | 2·28 | 0·96 | 0·97 |
| 0·1 | 31·8 | 0·925 | 0·94 |
| 0·2 | 155 | 0·89 | 0·70 |
| 0·5 | 269 | 0·82 | 0·30 |
| 1·0 | 236 | 0·74 | 0·15 |

* See para. 5.

(c) *Varying Concentration of Nitric Acid*

The effect of varying the nitric acid concentration is illustrated in Table 3. These results were obtained in experiments which were primarily directed towards the investigation of the efficiency of the backwashing of plutonium from carbon tetrachloride-TTA solution. Tracer plutonium was used. In a check of the rate of back-extraction it was found that equilibrium was achieved in a few minutes, and 15 min mixing was adopted as standard for backwashing experiments in which the plutonium was originally present in the organic phase.

The values of $K_{Pu}$ at higher acid concentrations are somewhat irregular. The concentration of plutonium in the organic phase was very low under these conditions, and adsorption effects may have interfered with the analysis. It will be noted that the efficiency of extraction of the plutonium back into the aqueous phase does not increase greatly at acid concentrations above about 8 M.

TABLE 3.—EFFECT OF VARYING NITRIC ACID CONCENTRATIONS IN THE SYSTEMS: (trace) Pu(IV)-0·2 M TTA in $CCl_4$—$HNO_3$ and (trace) Pu(IV)-0·5 M TTA in $C_2H_2Cl_4$—$HNO_3$

| $HNO_3$ molarity | $K_{Pu}$ (org/aq) | |
|---|---|---|
| | 0·2 M TTA/$CCl_4$ | 0·5 M TTA/$C_2H_2Cl_4$ |
| 1·0 | 150 | — |
| 1·41 | 8·8 | — |
| 3·24 | 0·27 | — |
| 4·6 | 0·052 | — |
| 4·95 | 0·047 | 0·039 |
| 6·5 | 0·0040 | 0·008 |
| 7·0 | 0·0035 | — |
| 7·9 | 0·0012 | 0·0078 |
| 8·1 | 0·0013 | — |
| 10·2 | 0·0027 | 0·004 |
| 11·9 | 0·0018 | 0·0032 |

## 4. BACKWASHING OF PLUTONIUM FROM TTA SOLUTIONS BY REDUCTION

As the figures for $K_{Pu}$ in Table 3 show, it is possible to backwash the plutonium from the solvent phase by forcing the equilibrium over in favour of the aqueous phase, using a high acid concentration. It might also be expected to be possible to carry out the back-extraction by stirring the solvent phase with a reducing agent. If the plutonium could be reduced to the trivalent state, the low distribution ratio for trivalent plutonium would cause it to concentrate in the aqueous phase.

Both hydroxylamine and hydrazine will reduce tetravalent plutonium to trivalent plutonium, and these reagents were stirred with tetrachlorethane-TTA solutions containing plutonium, with the results shown in Table 4.

TABLE 4.—THE REDUCTION OF PLUTONIUM IN THE SYSTEM 0·2 M TTA IN $C_2H_2Cl_4$

| Reducing agent | [acid] | Time of stirring min. | $K_{Pu}$ |
|---|---|---|---|
| Hydroxylamine hydrochloride 0·05 M | 0·5 N | 15 | 78 |
| | | 120 | 5·3 |
| | 1·0 N | 15 | 41 |
| | | 120 | 2·9 |
| Hydrazine nitrate 0·05 M | 1·0 N | 15 | 41 |
| | | 60 | 18 |
| | | 120 | 1·9 |
| | 2·0 N | 15 | 22 |
| | | 30 | 7·1 |
| | | 60 | 2·4 |
| | | 120 | 1·3 |
| | 3·0 N | 15 | 6·9 |
| | | 30 | 3·0 |
| | | 60 | 0·80 |
| | | 120 | 0·23 |
| Hydrazine nitrate 0·1 M | 1·0 N | 60 | 1·3 |
| Hydrazine nitrate 0·2 M | 1·0 N | 60 | 1·8 |
| Hydrazine nitrate 0·5 M | 1·0 N | 15 | 2·0 |
| | | 60 | 1·9 |
| | | 120 | 0·19 |

From these results it is clear that there is a slow step in the reaction. KING and REAS[11] have studied the equilibrium between TTA benzene and water, and concluded that over 90% of the TTA is present as the enol form in the organic phase, the remainder being present as ketone-hydrate. In the aqueous phase (which contains only about 2% of the TTA present) practically all the TTA is present in the hydrated keto form.

Reduction takes place in the aqueous phase, and the slow step in the reaction may be in the transfer of plutonium chelate across the interface, but is more likely to be due to some other factor which is not at present understood.

## 5. THE EQUILIBRIUM COEFFICIENT FOR TETRAVALENT PLUTONIUM

The equilibrium coefficient for the partition of tetravalent plutonium between organic and aqueous phases has been defined in equation (2). In this equation, the distribution ratio and the concentration of TTA are known for individual experiments. The values of the activity of nitric acid can be derived from Tables,[14] although

[14] LANDOLT-BÖRNSTEIN *Physikalisch-Chemische Tabellen*, Springer-Verlag, Berlin, 6th ed. 1952.

they are rather uncertain at high concentrations. The factor $f_{PuT_4}/f_{HT}^4$ can be derived from experimental results with varying TTA concentration, as indicated in Table 2. It will be seen that for the lower concentrations of TTA the "effective activity coefficient" $f_{HT}/\sqrt[4]{f_{PuT_4}}$ is close to that found by KING and REAS,[11] but decreases more rapidly at higher concentrations.

The factor $F = \alpha\gamma^5_{\pm Pu(NO_3)_2}[NO_3^-]^4$ cannot be evaluated directly, and for the present it is assumed that it remains substantially constant. It is on this basis that the values of $C' \times F$ are calculated in Table 5. Although there is no reason why this

TABLE 5.—CALCULATED VALUES OF THE EQUILIBRIUM COEFFICIENT FOR PLUTONIUM (IV)

| Solvent | Reagent concentrations | | | Pu distribution ratio | Equilibrium constant $C'$ (equation 2) ($\times$ '$F$') | Notes |
|---|---|---|---|---|---|---|
| | Pu (mg/ml) | $HNO_3$ (M) | TTA (M) | | | |
| | | | | | ($\times 10^6$) | cf. Table 2 |
| | | 1·0 | 0·2 | 150 | 1·1 | |
| | | 1·41 | 0·2 | 8·8 | 0·3 | |
| | | 3·24 | 0·2 | 0·27 | 0·6 | |
| | | 4·6 | 0·2 | 0·052 | 0·9 | |
| $CCl_4$ | | 4·95 | 0·2 | 0·047 | 13 | |
| | | 6·5 | 0·2 | 0·004 | 0·6 | |
| | Trace | 7·0 | 0·2 | 0·0035 | 0·9 | |
| | concn. | 7·9 | 0·2 | 0·0012 | 0·7 | |
| | $\sim 10^{-4}$ | 8·1 | 0·2 | 0·0013 | 0·9 | |
| | | 10·2 | 0·2 | 0·0027 | 0·8 | |
| | | 11·9 | 0·2 | 0·0018 | 16 | |
| | | 4·95 | 0·5 | 0·039 | 0·8 | |
| | | 6·5 | 0·5 | 0·008 | 1·0 | |
| $C_2H_2Cl_4$ | Trace | 7·9 | 0·5 | 0·0028 | 3·3 | |
| | | 10·2 | 0·5 | 0·0040 | 9 | |
| | | 11·9 | 0·5 | 0·0032 | 22 | |
| | 1·5 | 0·41 | 0·5 | 283 | 0·04 | |
| | 1·89 | 0·8 | 0·25 | 14 | 0·03 | |
| | 0·25 | 0·8 | 0·25 | 200 | 0·4 | |
| | 0·34 | 10·0 | 0·5 | 0·01 | 20 | Successive back-extraction from benzene |
| $C_6H_6$ | 0·04 | 10·0 | 0·5 | 0·001 | 2 | |
| | 0·001 | 10·0 | 0·5 | 0·001 | 2 | |
| | 1·97 | 10·0 | 0·5 | 0·022 | 44 | Successive back-extraction |
| | 0·006 | 10·0 | 0·5 | 0·007 | 14 | |
| | 3·33 | 8·0 | 0·25 | 0·007 | 3 | Successive back-extraction |
| | 0·59 | 8·0 | 0·25 | 0·007 | 6 | |
| $CCl_4$ | Trace | 1·0 | 0·02–1·0 | see Table 2 | $1·1 \times 10^6$ | Calculated value for Table 2 |

assumption should be correct, the fact that $C' \times F$ in Table 5 is fairly constant, is evidence that it is reasonable, although such constancy of $F$ is fortuitous.

It should be noted that only *total* plutonium distribution ratios have been measured. While an attempt was made in each experiment to ensure that the plutonium was in solution in the tetravalent state, it is difficult to ensure that this requirement is effectively satisfied. This is particularly true of experiments involving macro-amounts of plutonium (of the order of milligrams per millilitre), where disproportion and hydrolysis reactions are much more rapid.

Errors due to plutonium not being completely in the tetravalent state can be minimized by selecting data in which the partition coefficients do not depart too far from unity, e.g. in the range $10^{-2}$ to $10^{2}$. In this range, errors due to adsorption and contamination of samples are also less serious.

The factors just discussed should be taken into account in assessing the results which are listed in Table 5, which covers a wide range of acid and plutonium concentrations, and a variety of solvents. Considering the magnitude of the activity coefficient corrections which are involved, the values of $C' \times F$ are found to be surprisingly constant.

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Apart from a few measurements made with acid concentrations greater than 10 M, most of the calculated values of $C' \times F$ lie close to $1 \times 10^{5}$ for the trace experiments. On the other hand, the calculated values of the equilibrium coefficient for macro-amounts of plutonium are low for extractions in which the plutonium was initially present in the aqueous phase, and somewhat high for back-extractions in which the plutonium was initially in benzene-TTA solution. The low values are almost certainly due to the fact that the plutonium was not at all present as tetravalent plutonium.

In view of the complexity of the plutonium-TTA system, which includes the presence of both keto and enol forms in each phase, comparative studies with other solvents of the kind made by McKAY[15] may be expected to be of great assistance in the interpretation of TTA extraction data.

*Acknowledgements*—The experiments reported in this paper formed part of a programme of work which was carried out between September 1949 and November 1951 by the authors, assisted, for varying periods, by W. APPLETON, D. ELSON, R. LEWIS, Mrs. A. M. McCONNELL, G. NAISH, M. PYSDEN, A. WAIN, and Miss J. WELLS-COLE.

The authors are indebted to Mr. H. A. C. McKAY for helpful discussion of the paper.

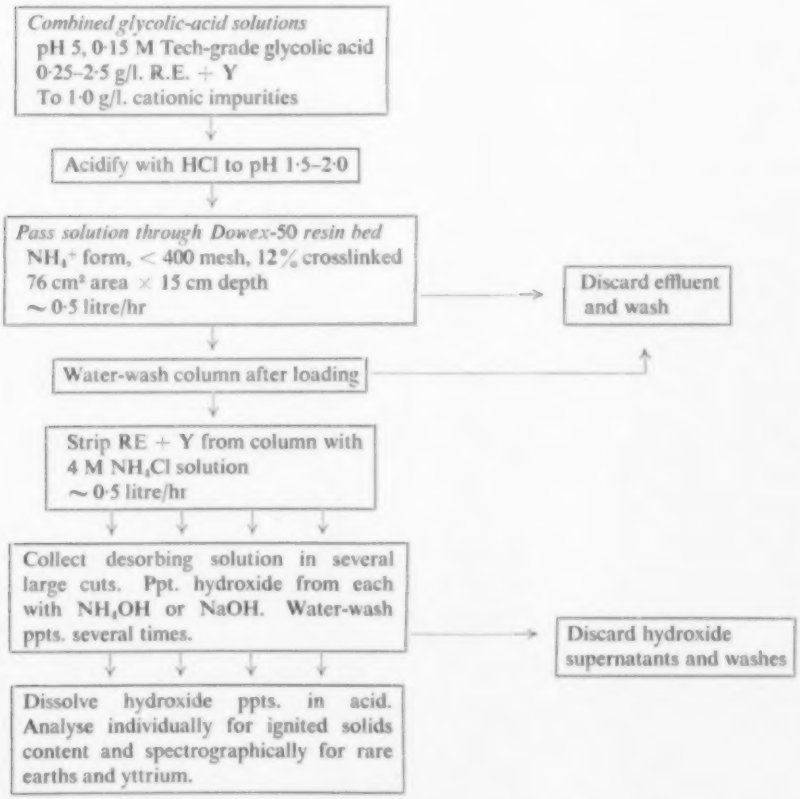
[15] H. A. C. McKAY To be published.

## Preparation of Rare-earth Concentrates*

(*Received* 19 *December* 1955)

A "CONCENTRATION and metathesis" ion-exchange resin column of the type described by COHN, PARKER, and TOMPKINS[1] was used recently at this laboratory to recover a quantity of mixed yttrium-group rare earths from several hundred litres of glycolic-acid solution. In applying this technique, when complex-forming anions such as citrate or glycolate are present, the first step of the recommended procedure is to acidify the solutions to suppress the ionization of the organic acid. The liquid is then passed through a small bed of cation-exchange resin where the cations are absorbed, while the complex-forming anions pass on through the bed in nonionized form and can be discarded. The rare earths are then stripped from the column by desorption by mass-action displacement, using a small volume of concentrated acid or salt solution to accomplish this purpose.

FIG. 1.—FLOWSHEET OF OPERATIONS


*Combined glycolic-acid solutions*
pH 5, 0·15 M Tech-grade glycolic acid
0·25–2·5 g/l. R.E. + Y
To 1·0 g/l. cationic impurities
Acidify with HCl to pH 1·5–2·0
*Pass solution through Dowex-50 resin bed*
$NH_4^+$ form, < 400 mesh, 12% crosslinked
76 cm² area × 15 cm depth
~ 0·5 litre/hr
Discard effluent and wash
Water-wash column after loading
Strip RE + Y from column with 4 M $NH_4Cl$ solution
~ 0·5 litre/hr
Collect desorbing solution in several large cuts. Ppt. hydroxide from each with $NH_4OH$ or NaOH. Water-wash ppts. several times.
Discard hydroxide supernatants and washes
Dissolve hydroxide ppts. in acid. Analyse individually for ignited solids content and spectrographically for rare earths and yttrium.

This general procedure was followed, the details being shown in Fig. 1. The degree of loading of the bed varied considerably from one recovery run to another, depending on the availability of solutions of like rare-earth composition suitable for combination. The maximum loading of rare

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

earth plus yttrium for a single run was 92 g (as oxide). This is about 70 to 75% of the calculated bed capacity for a starting mixture containing 50% yttrium.

This was essentially a salvage operation, and it was not originally anticipated that any marked separation of the individual rare earths would occur as a result of the relatively simple procedures involved. However, as a matter of convenience, the desorbing solution used to strip a given column was collected in several cuts or fractions and, when it was noted that the hydroxide precipitates formed in these separate cuts were different in appearance, their rare-earth distribution was estimated separately (spectrographically, by the copper-spark technique), rather than after recombination as had originally been intended. These analytical results (shown in Table 1) made it at once apparent that quite a useful degree of separation was, in fact, being attained. In recovery column No. 1, for example, where only two cuts were taken, over 97% of the ytterbium present was found in the first fraction, and over 95% of the dysprosium in the second. In both runs 2 and 3, the ytterbium was largely concentrated almost free of yttrium.

TABLE 1.—SPECTROGRAPHIC ANALYSES OF RECOVERY-RUN PRODUCTS

| Recovery column and cut number | Estimated per cent of total R.E. + Y in cut | Estimated composition of R.E. + Y fraction (per cent of element weight) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Y | Yb | Tm | Er | Ho | Dy | Tb | Gd |
| 1a | 53 | 30 | 45 | 5 | 18 | 1 | 1 | — | — |
| b | 47 | 60 | 1 | 0·5 | 5 | 2 | 28 | 3 | 0·1 |
| 2a | 34 | 1 | 94 | 4 | 1 | — | — | — | — |
| b | 66 | 41 | 14 | 4 | 28 | 1 | 11 | 0·3? | — |
| 3a | 62 | 2 | 81 | 6 | 9 | — | 0·6 | — | 1 |
| b | 12 | >20 | 12 | 6 | >20 | 3 | 0·1 | — | — |
| c | 26 | >20 | 3 | 2 | 25 | 8 | >20 | 3 | 1 |
| 4a | 36 | 80 | 0·6 | 2 | 10 | 2 | 6 | 0·1 | 0·3 |
| b | 32 | 74 | 0·1 | 1 | 6 | 2 | 15 | 0·6 | 1 |
| c | 23 | 65 | 0·04 | 0·4 | 4 | 3 | 22 | 3 | 4 |
| d | 9 | 30 | 0·01 | 0·1 | 2 | 2 | 30 | 5 | 30 |
| 5a | 3 | 80 | 0·6 | 2 | 16 | 1 | 0·2 | — | 0·6 |
| b | 60 | 81 | 0·1 | 0·7 | 6 | 2 | 8 | 0·4 | 0·8 |
| c | 25 | 71 | 0·02 | 0·3 | 5 | 2 | 18 | 2 | 3 |
| d | 7 | 71 | 0·007 | 0·1 | 2 | 1 | 18 | 2 | 5 |
| e | 5 | 33 | 0·005 | 0.07 | 2 | 2 | 29 | 4 | 29 |

Further examination of the data of Table 1 shows an apparent tendency in each run for a certain element to act as a "pivot," the position of this pivot presumably being determined by the composition of the original mixture of rare earths plus yttrium. Thus in recovery column No. 2, the percentage of thulium in each of the two cuts is essentially constant, whereas the heavier rare earths have concentrated in the first fraction, and those elements lighter than thulium in the second. In runs 1, 4, 5, holmium would appear to be the pivot, whereas in run 3 the pivot apparently falls between thulium and erbium.

The rare-earth separations obtained by the procedures sketched in Fig. 1 are relatively crude, but are still surprisingly effective in terms of the simplicity of the process and the small size of resin bed required. The method should be particularly useful in separating rare earths or groups of rare earths

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three or four units apart in atomic number to produce concentrates in a form well suited for final separations and purification procedures. Also, while iron, aluminium, and copper impurities (and presumably part of the singly-charged cations such as sodium and potassium) are absorbed onto the resin bed along with the rare earths from the original glycolic-acid solutions, they are stripped from the column either just ahead of, or just with, the first of the desorbed rare earths, so some purification from these contaminants can be easily obtained. This purification aspect of the process could probably be improved by adding additional steps, after the recommendations of COHN, PARKER, and TOMPKINS,[1] who employed a series of graduated-strength hydrochloric-acid washes selectively to desorb cationic impurities from rare-earth fission products absorbed on a similar resin column.

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[1] W. E. COHN, G. W. PARKER, and E. R. TOMPKINS *Nucleonics* **3**, 22 (Nov. 1948).

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# BOOK REVIEWS

**Handbuch der mikrochemischen Methoden, zweiter Band. Verwendung der Radioaktivität in der Mikrochemie** (in German). Edited by F. HECHT and M. K. ZACHERL. Vienna, Springer-Verlag, 1955. £6. 18. 0., $19.30.

THIS book is composed of three separate contributions: "Radiochemical Methods for Microchemistry" by E. BRODA and T. SCHÖNFELD; "The Measurement of Radioactivity in Microchemistry" by T. BERNERT, B. KARLIK, and K. LINTNER; and "Photographic Methods in Radiochemistry" by H. LAUDA.

The first of these sections occupies over two-thirds of the book and constitutes a comprehensive review of all analytical methods involving radioactivity. The material is carefully classified according to method and technique. This presents the subject in a novel way, although it does not lend itself to easy reference and is liable to lead to duplication. For instance, the procedure of using a radioactive material to mark the end point of a titration analysis is placed in a chapter headed "Analysis with Radioactive Reagents" but could nearly as well have been included in the chapter headed "Tracer Analysis"; again, the subject of coprecipitation has to be introduced several times. The arrangement is useful where the methods are unique, and leads, for instance, to a valuable section on neutron absorption and scattering as an analytical tool. However, refined modern methods such as ion exchange and chromatography using radioactive materials seem rather lost in the classification; so that, although they are mentioned, they scarcely receive the treatment that their importance warrants.

The section on the measurement of radioactivity consists only of three chapters, on ionization chambers, counters, and scintillators, contributed by the three authors respectively. This has led to some serious omissions. There is little to be found on modern techniques for precision counting using very thin films for mounting sources, and the corrections necessary in counting radioactivity from thick sources are inadequately described. In the section on radioactive decay nothing is included on the more complex decay and growth effects due to daughter products which so often confuse radioactivation analysis, and in the section on scintillators there is no description of the $\gamma$ spectrometer as a powerful tool for analysing mixtures of isotopes.

The final contribution on photographic methods deals with track recognition, measurement and counting, and autoradiography, as analytical tools. The theoretical aspects are only briefly considered, but the detailed practical technique and the sources of manufactured materials are fully discussed and make this perhaps the most valuable of the three parts of the book.

The whole book is admirably indexed, and the extensive references, which draw widely on European journals, are fully annotated. It is also a pleasure to note the beautiful printing and binding, which maintain the highest standards.

G. N. WALTON

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A. F. WELLS: **The Third Dimension in Chemistry.** Oxford University Press, 1956. 143 + xi pages. XIV plates. 21s. in United Kingdom.

THE author evidently enjoyed writing this book. It is not a treatise, nor yet an outline of its subject, though it might fairly be called an introduction; but it is an introduction from a novel starting-point. Its aim is to give the reader a new mental outlook in his approach to structural chemistry.

This accounts for the rather unusual choice of material. There is, for example, very little on crystallographic techniques. The approach is from topology, and the first three chapters deal

fascinatingly with polygons, polyhedra, and repeating patterns, respectively. Only in the fourth do we reach a discussion of symmetry properties, and only in the fifth and sixth are chemical structures treated other than incidentally. Even so, the chemical chapters—entitled "Ions and Ionic Crystals" and "Finite and Infinite Molecules"—seek to stimulate thought, rather than to cover the ground. The reader who wants more chemistry must refer to the author's well-known larger book.

The topological approach has the advantage that regular and distorted lattices are grouped naturally together, whereas their symmetry properties would put them into different classes. It should appeal to every reasonably mathematically-minded chemist.

My only criticism of the book is that the author has not quite made up his mind whom he is addressing. At times it seems to be an educated layman, as when he tells us how many chemical elements there are; but at other times, he seems to take for granted a considerable chemical background.

The book is well produced, and includes a valuable collection of stereoscopic photographs.

H. A. C. McKay

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 69 to 92. Pergamon Press Ltd., London

# HIGH-ENERGY EXCITATION FUNCTIONS IN THE HEAVY REGION*

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(*Received* 16 *April* 1956)

**Abstract**—The electrostatically deflected beam of the 184-inch cyclotron has been used with the stacked foil and absorber technique to determine the excitation functions for the following reactions: $Th^{232}(p, 6n)Pa^{227}$, $Th^{232}(p, 3n)Pa^{230}$, $Th^{232}(d, 7n)Pa^{227}$, $Th^{232}(\alpha, p8n)Pa^{227}$, $Th^{232}(\alpha, p5n)Pa^{230}$, and $U^{238}(p, \alpha 8n)Pa^{227}$. The data are presented graphically and discussed individually for each of the reactions. Some rough excitation function data have also been determined for the reactions $Th^{232}(d, 4n)Pa^{230}$, $U^{238}(p, \alpha 5n)Pa^{230}$, $Th^{232}(\alpha, 7n)U^{229}$, and $Th^{232}(\alpha, 6n)U^{230}$. The results are discussed in terms of compound nucleus formation, transparency effects, fission, and other factors in order to arrive at a qualitative picture for the mechanism of high-energy nuclear reactions with heavy nuclei.

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## 1. INTRODUCTION

IN the past, investigations of excitation functions with the bombarding particles from relatively low-energy accelerators[1] have led to a better understanding of low-energy nuclear reactions. Many precise measurements have been made in this study of the dependency of reaction yield upon bombardment energy.

The availability of high-energy particles makes it possible to extend this method of investigation to the energy region which is well beyond that of the binding energy of the individual nucleons. Excitation functions of a few light-element reactions with high-energy particles have been reported,[2] but those of heavy elements have not been investigated except for one determination by E. L. KELLY on the $Bi^{209}(\alpha, 2n)At^{211}$ reaction.[3]

During the course of work on the artificial collateral series[4, 5] produced in bombardments of thorium with deuterons and helium ions from the 184-inch cyclotron of the University of California Radiation Laboratory, we became interested in determining, through excitation functions, the energies for maximum yield of certain nuclides produced by spallation reactions. These preliminary experiments seemed to indicate that the transparency effect discussed by SERBER[6] is important in spallation

* Based in part on the PhD. thesis of W. W. MEINKE, University of California (Jan. 1950); also published as University of California Radiation Laboratory Declassified Report UCRL-483 (9 Nov. 1949). The present paper appeared as University of California Radiation Laboratory Report UCRL-868 (26 Sept. 1950), and is published essentially without change. The work was supported by the United States Atomic Energy Commission.

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(1) See, for example, E. T. CLARKE and J. W. IRVINE, JR. *Phys. Rev.* **69**, 680 (1946); E. L. KELLY and E. SEGRÈ *Phys. Rev.* **75**, 999 (1949); see also Appendix.

(2) See A. C. HELMHOLZ and J. W. PETERSON *Phys. Rev.* **73**, 541 (1948) abstr.; R. L. THORNTON and R. W. SENSEMAN *Phys. Rev.* **72**, 872 (1947); R. W. CHUPP and E. M. MCMILLAN *Phys. Rev.* **72**, 873 (1947); D. BOCKHOP, A. C. HELMHOLZ, S. D. SOFTKY, J. W. ROSE, and T. BREAKEY *Phys. Rev.* **75**, 1469 (1949) abstr.

(3) E. L. KELLY, University of California Radiation Laboratory Report UCRL-277 (Jan. 1949).

(4) A. GHIORSO, W. W. MEINKE, and G. T. SEABORG *Phys. Rev.* **74**, 695 (1948).

(5) ibid. **75**, 314 (1949).

reactions involving the heavy elements. It was also apparent from these early experiments that there is a definite trend toward lower absolute yields as more neutrons are expelled in the reaction leading to the product isotope.

In view of the value which excitation functions for heavy elements would have toward giving data to help in the understanding of high-energy nuclear reactions, and also because of the relative ease with which the yield of the alpha-emitting product nuclides can be quantitatively determined, it was decided to undertake the measurement of a number of such excitation functions. Included among the reactions which lend themselves to investigation are those in which large numbers of neutrons are emitted, such as the $(p, 6n)$ and $(d, 7n)$ reactions, and reactions in which charged particles are emitted together with neutrons, so that it seemed possible to study in some detail the interplay between compound nucleus formation and transparency effects at relatively high energies.

Although this work was completed and the present report written in 1950, publication was delayed because of some uncertainties in the energy scale of the bombarding particles and the lack of absolute values for some of the cross-sections, with the expectation that these shortcomings would be rectified with further work.

In view of the fact that the opportunity for further experimental work never presented itself and the feeling that the results are nevertheless useful and interesting, it was decided to publish the information at this time.

## 2. PROCEDURE

Stacked foils of 5-mil thorium (or uranium) metal with varying thicknesses of copper metal sandwiched between were bombarded with charged particles in the electrostatically deflected beam of the 184-inch frequency-modulated cyclotron. The first weighed foil intercepted the nearly-full-energy particles from the cyclotron (348-MeV protons, 194-MeV deuterons, or 388-MeV helium ions), and successive foils were struck by particles of decreasing energy until the entire beam energy had been expended in the foil stack. The energy of particles impinging on any one foil was determined by the use of range-energy relationships between the absorbing material and the particles.[7, 8] Since the decrease in energy of the high-energy particles in passing through each 5-mil foil is relatively small, the yields from such foils placed at selected points in a stack of copper absorbers define rather well a thin-target (differential) excitation function.

In each case, sixteen foils were placed at known energy positions in the stack. After bombardment, the 0·4-gram thorium (or 0·7-gram uranium) foils were removed and dissolved in portions of concentrated nitric acid (with ammonium fluorosilicate in the case of thorium). The 38·3-min $Pa^{227}$ and the 17-day $Pa^{230}$ isotopes are well suited for separation and characterization as reaction products. The element protactinium is easily and cleanly separated chemically from all other alpha-emitters produced in the bombardments. This simple protactinium chemistry also lends itself to a mass-production scheme which makes it possible to work up and have ready to

[6] R. SERBER *Phys. Rev.* **72**, 1114 (1947).
[7] W. A. ARON, B. G. HOFFMAN, and F. C. WILLIAMS, University of California Radiation Laboratory Report UCRL-121, 1st and 2nd revisions (1948, 1949); former also issued as U.S. Atomic Energy Commission Unclassified Document AECU-103 (Nov. 1948).
[8] These range-energy values and the experimental yield for each absorber position, as obtained in this work, are presented in detail in the Ph.D. thesis of W. WAYNE MEINKE, University of California (Jan. 1950).

count sixteen bombarded thorium samples in a short time (less than 2 hours). In the cases in which protactinium isotopes were to be measured, a protactinium fraction was separated by a solvent-extraction procedure involving simultaneous equilibration of the nitric-acid solution of each sample with a solution of thenoyltrifluoroacetone[9] (TTA) in benzene. The protactinium was thus extracted as a complex ion into the organic layer which was evaporated and flamed on thin, 1-inch-diameter platinum plates.

The alpha-particle activity was counted in a standard argon-filled ionization chamber in which the pulses from the electron collection were fed through a fast amplifier into a scale-of-512 counting circuit. When it was necessary to count beta particles, an end-window, alcohol-quenched, argon-filled Geiger-counter tube with a mica window ($\sim$3 mg/cm$^2$) was used in conjunction with a scale-of-64 counting circuit.

Immediately after bombardment and usually for about five hours thereafter, the 38·3-min isotope $Pa^{227}$ and its daughters present the predominant alpha activity in the pure protactinium chemical fractions. After a period of several weeks, the only prominent alpha activity is due to the $U^{230}$ series growing from the $Pa^{230}$ isotope. The radioactive purity of these samples was checked by alpha-particle decay measurements indicating the 38·3-min decay of the $Pa^{227}$, and, after other protactinium isotopes had decayed out, by alpha-particle pulse analysis for the $U^{230}$ series. A 48-channel alpha-particle pulse analyser[10] equipped with a fast sample-changing mechanism was used for the latter measurements. The observed counting rates were corrected for decay or daughter growth, target weight, etc., converted to disintegrations per minute at the end of bombardment, and plotted against the bombarding energy for each sample, thus giving the excitation function for the particular reaction studied.

Absolute chemical yields were not determined, but since all samples in a run were worked up simultaneously with the same chemical procedure used on each sample, the relative chemical yields are accurate to within about 5%. The calculated energy values used for these excitation functions are only approximate, particularly at the lower end of the energy scale, because of beam straggling and the spread in initial energy of the particles in the 184-inch cyclotron, as discussed more fully later. Consequently, while maximum yield and threshold-energy values observed from the experimental curves may be considerably in error on the absolute-energy scale, they should be significant when considered in relation to the rest of the excitation-function curve.

The experimental techniques used in the work are discussed more thoroughly in a later section (Section 5).

## 3. RESULTS

Excitation functions were obtained for the ($p$, $6n$) and ($p$, $3n$) reactions on thorium, the ($p$, $\alpha 8n$) and ($p$, $\alpha 5n$) reactions on uranium, the ($d$, $7n$) and ($d$, $4n$) reactions on thorium, and the ($\alpha$, $p8n$) and ($\alpha$, $p5n$) reactions on thorium as well as rough data for some ($\alpha$, $xn$) reactions on thorium. The bombardments were usually of about 90-min duration, and the plotted disintegration rates are corrected for decay back to the end of the bombardment. Usually at least two runs were made for each reaction. The data are presented graphically for most cases and discussed individually for each of

[9] J. C. Reid and M. Calvin, U.S. Atomic Energy Commission Declassified Document MDDC-1405 (Aug. 1947); also *J. Amer. Chem. Soc.* **72**, 2948 (1950).

[10] See A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd National Nuclear Energy Series, Plutonium Project Record, Vol. 14B. *The Transuranium Elements: Research Papers*, Paper No. 17.3 (McGraw-Hill Book Co., Inc., New York, 1949).

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the reactions in the following sections. The yields below the thresholds are due to the fact that a few particles of high energy reach the target by coming in through the side of the stack of absorber foils except in some cases such as the $Al^{27}(d, \alpha p)Na^{24}$ reaction, where these yields are mostly due to neutron background.

(*a*) *Protons*

1. $Th^{232}(p, 6n)Pa^{227}$. The results of two different bombardments in which this reaction was studied are plotted in Fig. 1. The points fall on a smooth curve whose

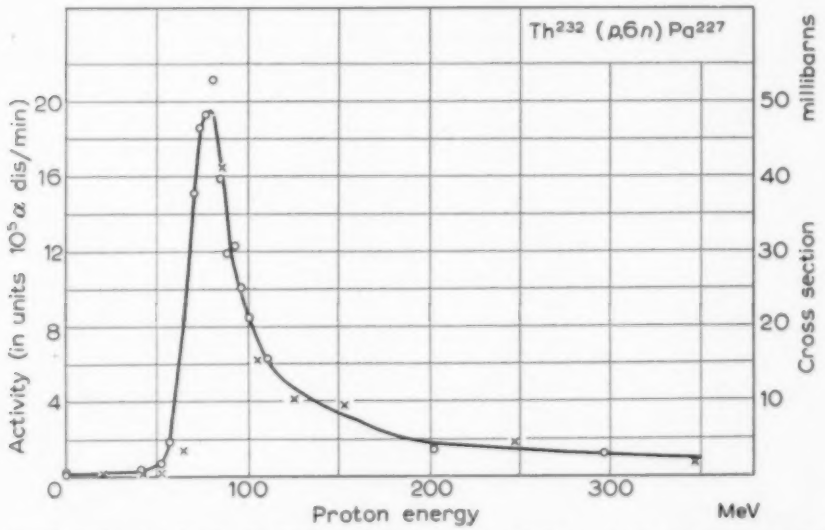


FIG. 1.—Excitation function for the $Th^{232}(p, 6n)Pa^{227}$ reaction. Circles represent run I; crosses, run II. (The apparent yield below the threshold energy shown in this and following figures is due to a small fraction of the incident beam striking the stack of foils from the side. Also, the energy scale in this and the following figures is very approximate because of the spread in initial energy of the incident particles and straggling in the stacked foils.)

maximum rises a factor of almost 20 above the yield value at full energy (348 MeV). The range of the protons is sufficiently great to make necessary the proper corrections for nuclear absorption, and these have been made as described later (Section 5b). Corrections for loss of beam due to scattering could not be made with the uncollimated proton beam. The curve is not drawn through the point at 80 MeV, even though this point would appear to be at the peak of the excitation function. When counted later for $U^{230}$, this sample gave a yield value which was definitely displaced from the curve for the $(p, 3n)$ reaction (see Fig. 3). Possibly some error in aliquot measurements caused the discrepancy. In Fig. 2 the peak of the curve is plotted on an enlarged scale to show the extent of the symmetry involved. It can be seen that on the high-energy side of the peak another mode of reaction becomes apparent and is superimposed on a somewhat symmetrical peak.

A single experiment in which the collimated external proton beam was used gave a value of about $2{\cdot}5 \times 10^{-3}$ barns as the absolute cross-section for this reaction at full energy (348 MeV). The experimental details are given later. From this cross-section value we see that the cross-section at the peak of the curve should be about $5 \times 10^{-2}$ barns. Because of the questionable chemical yield discussed later on (Section 5d),

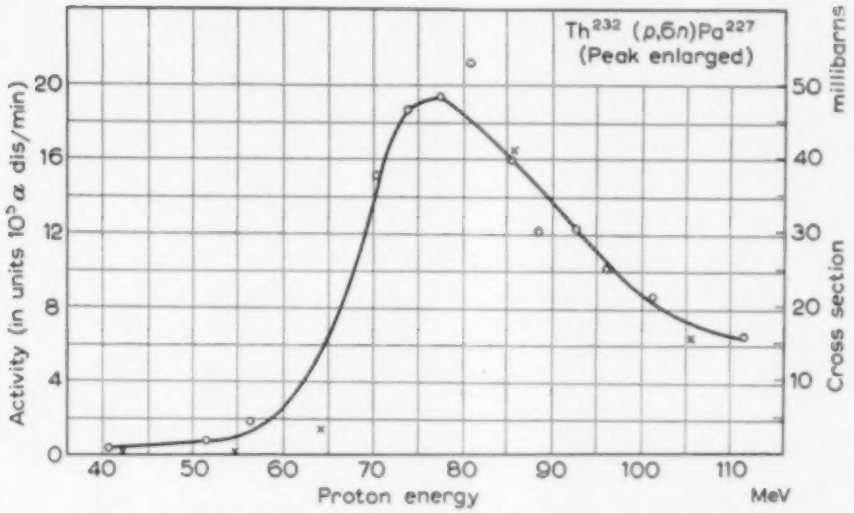


FIG. 2—Excitation function for the $Th^{232}(p, 6n)Pa^{227}$ reaction on enlarged scale. Circles represent run I; crosses, run II. Absolute value of energy scale not accurate (see text).

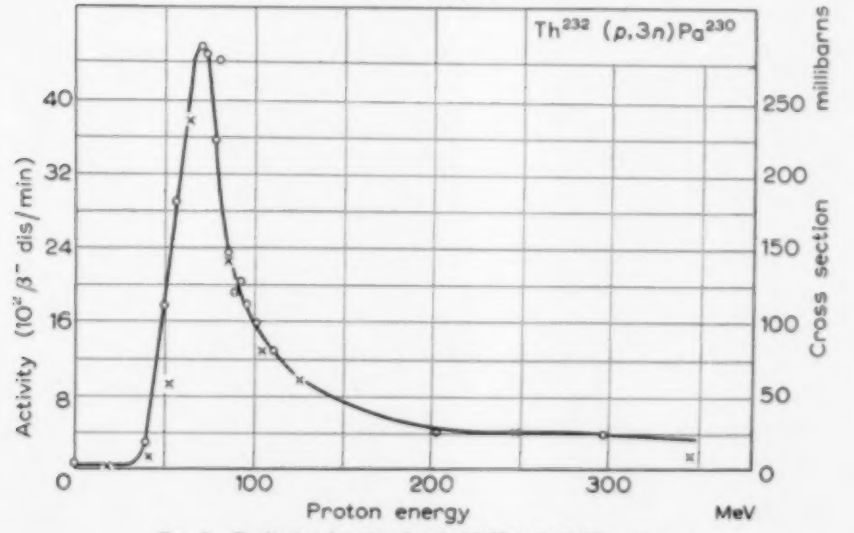


FIG. 3.—Excitation function for the $Th^{232}(p, 3n)Pa^{230}$ reaction. Circles represent run I; crosses, run II.

this can only be considered the maximum value for the cross-section, further experiments being necessary to establish the true value. It may be pointed out that the measured cross-section at the peak is lower than the true maximum cross-section, because of the energy-spread effect. This effect is discussed in Section 5b. Similar corrections apply also to the other peak cross-sections mentioned later.

2. *$Th^{232}(p, 3n)Pa^{230}$.* The yield values for the reaction $Th^{232}(p, 3n)Pa^{230}$ are plotted in Fig. 3. Here again a factor of about 20 between the maximum yield and the yield at full energy is found.



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A very interesting observation can be made from the curves for the $(p, 6n)$ and $(p, 3n)$ reactions on thorium. Although the curves for the two reactions have a similar shape and a comparable ratio of peak yield to full energy yield, there is a difference in absolute yield of about 5 between the two, in favour of the $(p, 3n)$ reaction. This difference was found by determination of the number of atoms formed by each reaction at the peak of the excitation function. The ratios of about 10% beta-decay branching[11] for $Pa^{230}$ and about 85% alpha-decay branching[4] for $Pa^{227}$ were used in the calculations. By using this factor of 5 and the yield mentioned in the previous section, it follows that at the peak of its excitation function, the absolute cross-section for the $(p, 3n)$ reaction is about 0·25 barns.

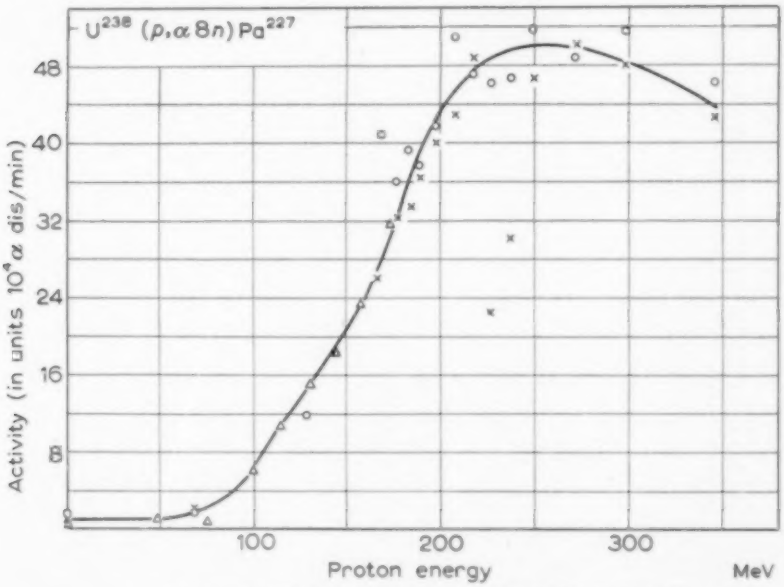


FIG. 4.—Excitation function for the $U^{238}(p, \alpha 8n)Pa^{227}$ reaction.
Circles represent run I; crosses, run II; and deltas, part of run III.

As described in a recent publication, H. A. TEWES (*Phys. Rev.* **98,** 25 (1955) has measured the excitation function for this same reaction $Th^{232}(p, 3n)Pa^{230}$ more accurately and found a peak cross-section of approximately 0·5 barns at about 25 MeV. Since the energy of his protons are known accurately, his results fortunately can be used as a calibration for the low-energy part of the proton-energy scale used in this paper; thus the peaks in Figs. 1–4 should be shifted to lower energies.

3. *$U^{238}(p, \alpha 8n)Pa^{227}$.* In addition to the thorium bombardments, the protactinium fraction was separated from pieces of 5-mil uranium foil, bombarded under the same conditions as the thorium foil. The results of these uranium bombardments are given in Fig. 4. Considerable trouble was encountered in the attempts to develop chemical procedures which would give consistent chemical yields for all of the sixteen foils in a bombardment. This trouble is reflected in the somewhat larger scattering of yield values for this reaction than for the reactions in thorium bombardments. Despite the

[11] M. H. STUDIER and R. J. BRUEHLMAN, as listed by G. T. SEABORG and I. PERLMAN *Rev. Mod. Phys.* **20,** 585 (1948).

scattering, however, the points do define a very broad peak near the high-energy portion of the curve.

4. $U^{238}(p, \alpha 5n)Pa^{230}$. Too little activity was available from the reaction $U^{238}(p, \alpha 5n)Pa^{230}$ to make it feasible to obtain a definitive yield curve. The points obtained scattered much more than for the above reaction, but did define a broad peak which was near the high-energy portion of the curve but displaced somewhat to the low-energy side of the $(p, \alpha 8n)$ curve. The ratio of yields for the two reactions at the peaks of their excitation functions is about 6 or 7 in favour of the $(p, \alpha 5n)$ reaction.

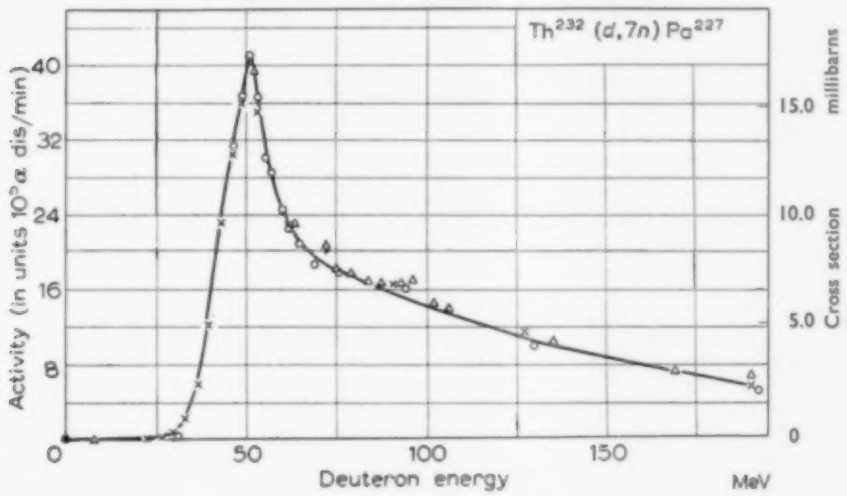


FIG. 5.—Excitation function for the $Th^{232}(d, 7n)Pa^{227}$ reaction. Circles represent run I; crosses, run II; and deltas, run III.

(*b*) *Deuterons*

In the $(d, xn)$ reactions, as in the $(p, xn)$ reactions, excitation functions with definite sharp peaks are found, even when as many as seven neutrons are emitted. The range of full-energy deuterons (194 MeV) from the 184-inch cyclotron is about 2·5 cm in copper, and although the nuclear absorption has not been measured, the corrections would certainly be less than those made in the proton bombardments. Corrections for loss of the collimated deuteron beam due to scattering were not made, but would be small (the order of 15–20%). The total beam current available with the deuteron beam of the large cyclotron is roughly equal to that of the proton beam.

1. $Th^{232}(d, 7n)Pa^{227}$. The yields for the reaction $Th^{232}(d, 7n)Pa^{227}$ are plotted in FIG. 5. The reaction-yield curve rises to a very definite peak which represents about eight times the yield value at full energy. An enlarged plot of the peak of this excitation curve is shown in Fig. 6. Using the same methods as for the $(p, 6n)$ reaction, absolute cross-section determinations for this reaction were made. The average of values obtained with full energy deuterons is $2{\cdot}3 \times 10^{-3}$ barns, making the cross-section at the peak of the curve about $1{\cdot}8 \times 10^{-2}$ barns. This value is probably accurate to within 15%.

2. $Th^{232}(d, 4n)Pa^{230}$. In these thorium bombardments, unfortunately, the energy values which were chosen so as to obtain an outline of the peak for the $(d, 7n)$

excitation function are not suitable to outline completely the peak of the curve for the reaction $Th^{232}(d, 4n)Pa^{230}$. The position of the points makes it possible to observe only the high-energy slope of this peak. From these experimental points, however, we can set a lower limit of about 4 for the ratio of total atoms $Pa^{230}/Pa^{227}$ formed at the peaks of the yield functions.

3. $Th^{232}(d, 7n)Pa^{227}$, $Al^{27}(d, \alpha p)Na^{24}$, and $C^{12}(d, n)N^{13}$. In an effort to determine more accurately the threshold energy for the $(d, 7n)$ reaction on thorium, simultaneous bombardment of thorium, aluminium, and carbon (as polystyrene) foils was attempted.

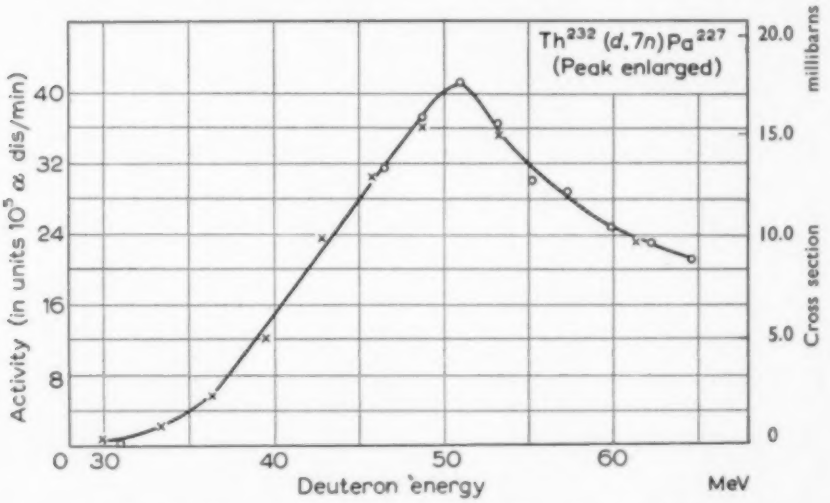


FIG. 6.—Excitation function for the $Th^{232}(d, 7n)Pa^{227}$ reaction on enlarged scale. Circles represent run I; and crosses, run II. Absolute value of energy scale not accurate (see text).

The excitation functions for the $(d, \alpha p)$ reaction on aluminium[12] and the $(d, n)$ reaction[13] on carbon had been previously studied at low energies, and it was thought that the determination of the threshold values for these reactions in stacked foils in the 184-inch cyclotron might establish a low-energy anchor point for the excitation-function energy scale. Fig. 7 presents the results of the simultaneous determination of these three excitation functions from a bombardment of one hour and forty-five minutes duration. In this case the abscissae are given in thickness of aluminium absorber rather than energy because of the uncertainty of the latter near the end of the range of the deuterons. Chemical separations were not needed in the case of the aluminium and polystyrene targets.

Unfortunately, straggling and the initial energy distribution of the deuteron beam makes an exact interpretation of these experimental threshold values difficult. It can only be said that the difference in threshold between the $C^{12}(d, n)N^{13}$ reaction (which occurs at about 2 MeV) and that of the reaction $Th^{232}(d, 7n)Pa^{227}$ amounts to about 1200 mg/cm² of aluminium for the range of the deuteron, which corresponds[7] very roughly to an energy of about 40 MeV for the threshold of the latter reaction.

[12] E. T. CLARKE *Phys. Rev.* **71**, 187 (1947).
[13] H. W. NEWSON *Phys. Rev.* **51**, 620 (1937).

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(*c*) *Helium Ions*

The determination of excitation functions for bombardments with helium ions is more difficult, since the beam current in the 184-inch cyclotron is only about one-tenth that obtained for protons and deuterons. In addition, for all reactions other than the (α, *xn*) reactions, there is the possibility that deuteron contamination of the helium-ion beam can produce the activity in question by another favourable reaction, and consequently obscure the yield of the reaction under study. The (α, *pxn*) reactions producing protactinium isotopes from thorium were studied in bombardments in which a half-inch stack of copper foils was required to absorb completely the helium-ion beam. A few experiments were also made with the (α, *xn*) reactions.

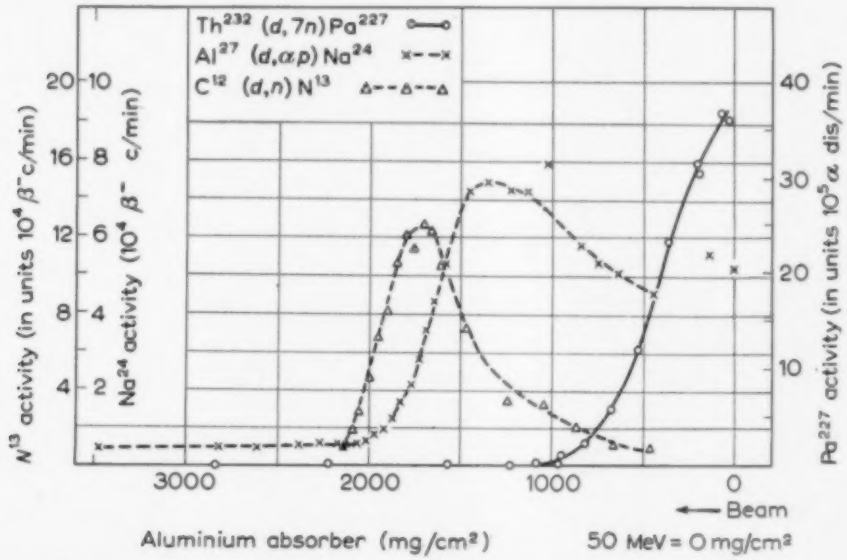


FIG. 7.—Excitation functions for the $Th^{232}(d, 7n)Pa^{227}$, $Al^{27}(d, \alpha p)Na^{24}$, and $C^{12}(d, n)N^{13}$ reactions obtained in a single bombardment with 194-MeV deuterons reduced in energy by copper absorbers to about 50 MeV (represented as 0 mg/cm² Al).

1. *$Th^{232}$(α, p8n)$Pa^{227}$*. Fig. 8 shows the yield values for $Pa^{227}$ obtained from a bombardment of thorium with helium ions. This curve shows no sharp peak.

2. *$Th^{232}$(α, p5n)$Pa^{230}$*. Fig. 9 shows a companion curve to the one above obtained for the (α, *p5n*) reaction in the same bombardment. In these (α, *pxn*) curves the peak yield for the (α, *p5n*) reaction is greater by a factor of about 7 than that for the (α, *p8n*) reaction.

3. *$Th^{232}$(α, xn) reactions*. Insufficient 20·8-day $U^{230}$ or 58-min $U^{229}$ alpha activity was formed in bombardments of stacked foils with the electrostatically deflected beam to permit accurate determination of the (α, 6*n*) or (α, 7*n*) excitation functions. In addition, the chemical procedures required to obtain pure uranium samples from the bombarded material were not adaptable to the mass-production methods employed in the protactinium separations. Consequently, the only definitive experiments have been individual bombardments of thorium foils at different radii (and hence different energies) in the internal cyclotron beam without the benefit of a monitor but with

conditions of each bombardment as nearly equivalent as possible. These experiments indicate that the $(\alpha, xn)$ excitation functions exhibit sharp peaks of about the same

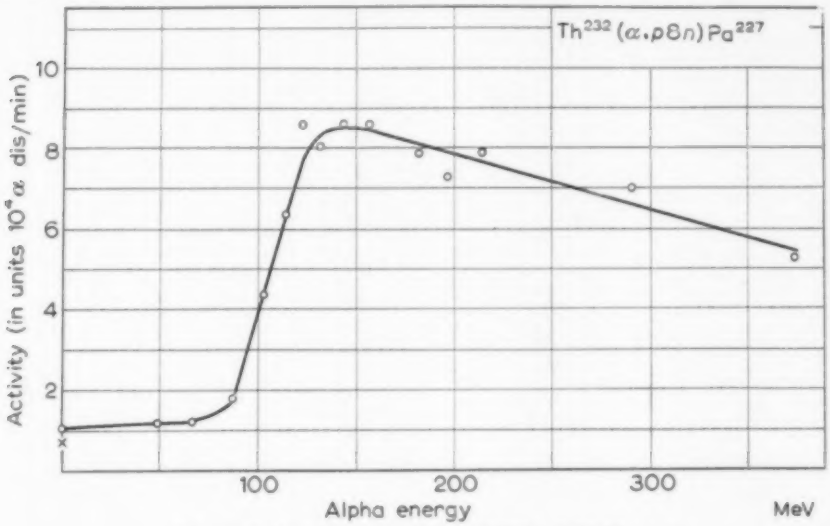


FIG. 8.—Excitation function for the $Th^{232}(\alpha, p8n)Pa^{227}$ reaction.

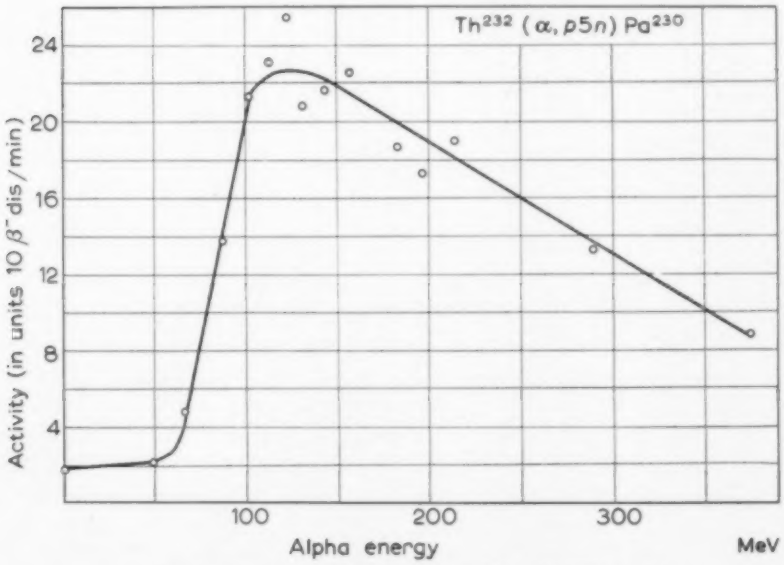


FIG. 9.—Excitation function for the $Th^{232}(\alpha, p5n)Pa^{230}$ reaction.

width as that of the peak in the yield curve for the $(p, 6n)$ reaction. The shape of the curve beyond the high-energy side of the peak has not yet been determined.

## 4. DISCUSSION

The data presented in the foregoing figures are unfortunately rather rough, due to the difficulty of the experimental procedures and more especially to the unavoidable

limitations placed by the spread of energy in the particle beams delivered by the 184-inch cyclotron. Corrections for scattering and nuclear absorption were not applied (except in the case of protons, where the latter correction was made). Nevertheless, the data give some interesting and in some cases rather surprising information on the mechanism of nuclear reactions in which relatively large numbers of nucleons are expelled. Comparable information on such reactions had not been obtained hitherto, and therefore even rather rough data are of interest.

The excitation function shown in Fig. 1 for the ($p$, $6n$) reaction shows a surprisingly sharp peak. The width at one-half maximum, uncorrected for the spread in energy of the protons, is some 25 MeV, and should probably be noticeably less than this if correction could be made for the unknown spread in energy of the initial 348-MeV protons (the possible magnitude of this spread and that due to straggling is discussed briefly further on in Section 5b). This seems to indicate that even at energies as high as some 50 to 75 MeV, the mechanism of reaction involves the formation of a compound nucleus similar to that which forms such a successful model for explaining the course of reactions at lower energies. The sharpness of this peak may be due to the fact that a heavy nucleus is involved, and perhaps is not to be expected in the case of the ($p$, $6n$) reaction with much lighter nuclei. The ($p$, $3n$) and the ($d$, $7n$) reactions, presented in Fig. 3 and Fig. 5, also show sharp peaks, but this is not surprising in the case of the former.

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The effect of nuclear transparency does show up at the higher energies where appreciable yields of all three of these reactions are found. This can be explained by the mechanism discussed by SERBER,[6] in which energies much smaller than the total energy of the incident projectile are obtained from it and utilized by the struck nucleus. This mechanism apparently becomes important at energies sufficiently high for the collision time between the incident particle and a nucleon in the nucleus to be short compared to the time between collisions of the nucleons in the nucleus. The first step in such a high-energy nuclear reaction probably involves a collision between the incident particle and an individual nucleon, and the amount of energy transferred to the nucleus depends on the number of subsequent collisions of this type and the further collisions of the struck nucleons with other particles in the nucleus. This leads to a wide distribution of excitation energies of the struck nucleus. As a consequence, an appreciable fraction of struck nuclei are excited to a given energy, say 50 to 75 MeV, even when the incident particles vary in energy from some 100 to 350 MeV, thus supplying the nucleus with the optimum energy and accounting for the continuing high yields of reactions like the ($p$, $6n$) and ($d$, $7n$). The fact that the relative yield of the reaction at high energies compared to the peak yield with deuterons somewhat exceeds the same ratio for the reaction with protons may be connected with the fact that the high-energy deuteron has its energy divided between its two nucleons and is therefore better suited for the transfer of small amounts of energy to the struck nucleus than is the proton. On the other hand, this difference may be caused entirely by the greater straggling and initial energy distribution of the proton beam causing "smearing out" of the peak.

It may be of some interest to make a more quantitative comparison between the observed peaks of the excitation curves for the ($p$, $6n$) and ($d$, $7n$) reactions and what would be predicted on the basis of the compound-nucleus idea.

When the excitation of the nucleus is as large as 50 MeV or more, the number of

possible competing processes is quite large. For some of the competing processes such as those involving emission of charged particles, one can estimate the corresponding probabilities in a rough way. With 60-MeV excitation, for example, the nuclear temperature of a heavy nucleus like thorium is perhaps about 3 MeV, the Coulomb barrier $E_c$ for emission of a proton is about 15 MeV. This means that the emission of a proton is at a disadvantage with respect to the emission of a neutron by a factor of the order of $e^{-E_c/T} = e^{-5} \approx 1/150$. We have therefore neglected competition from proton emission entirely, and for stronger reasons that from deuteron or alpha-particle emission. A big unknown in the problem, however, is competition from fission. We know for certain that this competition is important. Indirect evidence on this is also obtained from the relatively low value of the peak cross-section for the $(p, 6n)$ and $(d, 7n)$ reaction; it is clear that, at the energy corresponding to the peak, a large fraction of the total cross-section is devoted to fission. The overall importance of fission is no doubt increased by the fact that fission has a chance to compete with the $(p, xn)$ and $(d, xn)$ processes at each successive evaporation of a neutron. Thus a possible, though arbitrary, interpretation of the results is obtained on the assumption of a *constant* ratio $r$ between neutron width and fission width. The measured ratio of 5 between the heights of the Th$(p, 3n)$ and Th$(p, 6n)$ peaks, or what is about the same, between the areas under the two peaks, gives for $r$ the value $1/(5^{+1/3} - 1)$ which is close to unity, a result strikingly similar to those obtained from experiments at lower excitation energies.

If the ratio $r$ is constant, it is clear that the existence of fission will affect the absolute cross-section *but not the shape* of the excitation function for a $(p, xn)$ or $(d, xn)$ process. The crude calculations described below are made, therefore, neglecting fission altogether.

Other interpretations are no doubt possible. One may assume, for example, that the probability of emission of a neutron increases much more rapidly, with increasing excitation energy, than fission probability. In this case fission competes with neutron emission only in the last stages of the evaporation process, and the number of times such effective competition takes place is independent of the number of evaporations. In this case the lower yield of the $(p, 6n)$ process with respect to the $(p, 3n)$ process would be attributed to the increased fissionability of the nuclei present during the last stages of the evaporation process; this increased fissionability is expected owing to the decrease in the number of neutrons (increase of the $Z^2/A$ ratio).

We do not think that the shape of the excitation curve for, say, a $(p, 6n)$ process will depend in a critical manner on the assumed dependence of the fission probability on energy. In view of the present uncertainty about that dependence, it would not be worth while to explore in detail the various possibilities.

In the above-mentioned case, in which one may forget fission, the problem is fairly simple. We may assume that the probability distribution for the kinetic energy $\varepsilon_n$ of the $n$th neutron is given approximately by a Maxwellian law: $\varepsilon e^{-\varepsilon/T}\, d\varepsilon$, with a temperature $T$ determined by the residual excitation of the nucleus after $n - 1$ neutrons are emitted. For a heavy nucleus we assume $T \approx 0{\cdot}4E^{1/2}$, where $E$ is the excitation energy ($T$ and $E$ both in MeV). The average value and mean square deviation of $\varepsilon$ are then:

$$\langle \varepsilon \rangle = 2T; \quad \langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = 2T^2 \tag{1}$$

For large values of $\varepsilon$, the Maxwellian law fails, and a far better approximation is given

by WEISSKOPF's formula $\varepsilon e^{S(E')}d\varepsilon$, $S(E')$ being the entropy of the nucleus after the evaporation. Here $E'$ is the excitation energy after the neutron is emitted, $E' = E - B - \varepsilon$, if $B$ is the binding energy of the neutron which for simplicity we regard as independent of $n$. It is easy to see that this modification can be approximately taken into account by using for the temperature $T$ in equation (1) the temperature evaluated for an excitation $E - B$, i.e. $T \approx 0{\cdot}4(E - B)^{1/2}$, i.e. roughly speaking, the temperature *after* the evaporation rather than before.

Our problem is, of course, to find the probability of emission of $x$, and no more than $x$, neutrons. This is given by $P(x) - P(x + 1)$, where $P(x)$ is the probability of emission of at least $x$ neutrons, or, in other words, the probability that the first $x - 1$ neutrons are emitted with energies $\varepsilon_1, \ldots, \varepsilon_{x-1}$ satisfying the condition

$$E_0 - (x - 1)B - \varepsilon_1 - \ldots - \varepsilon_{x-1} > B \tag{2}$$

where $E_0$ is the initial excitation energy. This is the condition that there be enough energy left for the evaporation of at least another neutron. Knowing the probability distribution of $\varepsilon_1, \varepsilon_2, \ldots$, we can estimate the probability that (2) is satisfied. If $\eta = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_{x-1}$, and $f(\eta)\,d\eta$ is the distribution law for $\eta$, we have

$$P(x) = \int_0^{E_0 - xB} f(\eta)\,d\eta. \tag{3}$$

So we must first find $f(\eta)$. This is given by a very complicated integral, but we know from general theorems that if $x$ is fairly large, one can use "asymptotic" laws, such as the Gauss or the Poisson distribution law. Both laws involve only two arbitrary parameters, which can be expressed in terms of the average value

$$\langle\eta\rangle = \langle\varepsilon_1\rangle + \ldots + \langle\varepsilon_{x-1}\rangle \tag{4}$$

and the mean-square derivation

$$\sigma^2 = \langle(\eta - \langle\eta\rangle)^2\rangle = \sum_{n=1}^{x-1}\langle(\varepsilon_n - \langle\varepsilon_n\rangle)^2\rangle + 2\sum_{n=1}^{x-1}\sum_{m=1}^{n-1}\langle(\varepsilon_n - \langle\varepsilon_n\rangle)(\varepsilon_m - \langle\varepsilon_m\rangle)\rangle. \tag{5}$$

When the root-mean-square deviation $\sigma$ is small compared to $\langle\eta\rangle$, the difference between the Gauss and the Poisson law is negligible, but the latter, i.e.

$$f(\eta)\,d\eta = [s^s/\Gamma(s)]\,(\eta/\langle\eta\rangle)^{s-1}e^{-s\eta/\langle\eta\rangle}d\eta/\langle\eta\rangle \tag{6}$$

$$s = \langle\eta\rangle^2/\sigma^2 \tag{7}$$

is preferable, since GAUSS's law extends to negative values of $\eta$, which are physically meaningless. Once the average values (4) and (5) are known, the exponent $s$ is given by (7), and we can evaluate the integral (3) by means of a table of the incomplete gamma function.

The main remaining difficulty is that the variables $\varepsilon_1, \varepsilon_2, \ldots$, are statistically dependent, since the temperature for $\varepsilon_2$ depends on $\varepsilon_1$, the temperature for $\varepsilon_3$ depends on $\varepsilon_1 + \varepsilon_2$, etc .... The difficulty, however, can be circumvented by a recurrent procedure, in which use is made of the fact that the temperature $T$ is a slowly variable function of the excitation energy. Thus if

$$\zeta = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_x = \eta + \varepsilon_x,$$

we have

$$\langle\zeta\rangle = \langle\eta\rangle + \langle\varepsilon_x\rangle = \langle\eta\rangle + 2\,\langle T\rangle$$

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where $T$ is now the temperature for the emission of the $x$th neutron or, according to our previous discussion,

$$T = T(\eta) = 0{\cdot}4(E_0 - xB - \eta)^{1/2}. \tag{8}$$

As a first approximation we may set $\eta = \langle\eta\rangle$ in (8) and obtain a $T(\langle\eta\rangle) = T_1$, say. Then expanding (8) in powers of the difference $\eta - \langle\eta\rangle$:

$$T(\eta) = T(\langle\eta\rangle) + (dT/d\eta)(\eta - \langle\eta\rangle) + 1/2(d^2T/d\eta^2)(\eta - \langle\eta\rangle)^2 + \ldots \tag{9}$$

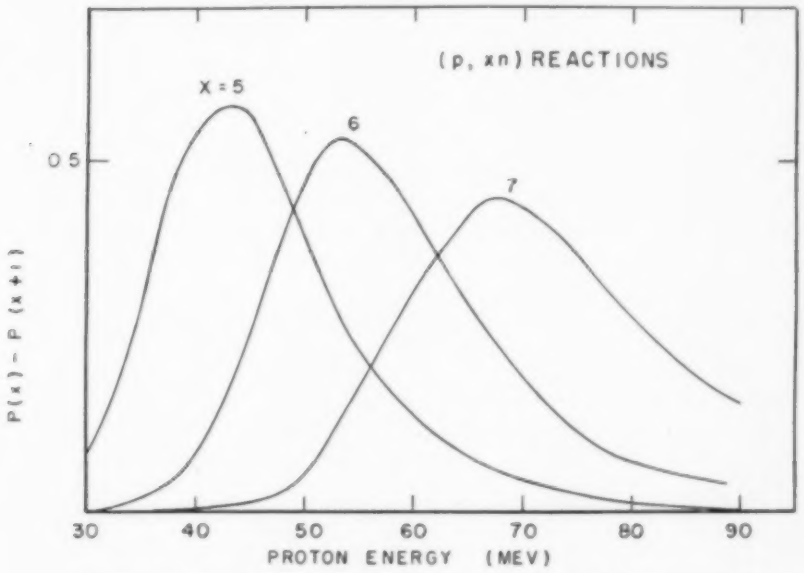


FIG. 10.—Probability of emission of $x$ neutrons after capture of a proton. For deuterons, decrease the energy values by 4 MeV.

Now, to obtain $\langle\varepsilon_x\rangle$ according to equation (1) we must take twice the average of (9). In this manner we obtain finally

$$\langle\zeta\rangle = \langle\eta\rangle + 2T(\langle\eta\rangle)\{1 - \langle(\eta - \langle\eta\rangle)^2\rangle/(E_0 - xB - \langle\eta\rangle)^2\}. \tag{10}$$

In a similar manner we compute

$$\langle(\zeta - \langle\zeta\rangle)^2\rangle = \langle(\eta - \langle\eta\rangle)^2\rangle + \langle(\varepsilon_x - \langle\varepsilon_x\rangle)^2 + 2\langle(\eta - \langle\eta\rangle)(\varepsilon_x - \langle\varepsilon_x\rangle)\rangle. \tag{11}$$

For instance, in the last term, we again used the fact that $\langle\varepsilon_x\rangle$ is $2T(\eta)$ averaged over $\eta$, and write

$$\varepsilon_x - \langle\varepsilon_x\rangle = \varepsilon_x - 2T(\eta) + 2T(\eta) - \langle\varepsilon_x\rangle. \tag{12}$$

Then

$$\langle(\eta - \langle\eta\rangle)(\varepsilon_x - \langle\varepsilon_x\rangle)\rangle = \langle(\eta - \langle\eta\rangle)(\varepsilon_x - 2T(\eta))\rangle + \langle(\eta - \langle\eta\rangle)(2T(\eta) - \langle\varepsilon_x\rangle)\rangle. \tag{13}$$

The averaging can be done first over $\varepsilon_x$ for a given $\eta$, then over $\eta$. The first term on the right of equation (13) is zero, the second is evaluated expanding $T(\eta)$ as before. Finally one gets

$$\langle(\zeta - \langle\zeta\rangle)^2\rangle = \langle(\eta - \langle\eta\rangle)^2\rangle + 2T^2(\langle\eta\rangle) - \langle(\eta - \langle\eta\rangle)^2\{2T(\langle\eta\rangle)(E_0 - xB - \langle\eta\rangle)^{-1} - T^2(\langle\eta\rangle)(E_0 - xB - \langle\eta\rangle)^{-2}\}. \tag{14}$$

Equations (10) and (14) allow one to compute the average and standard deviation of $\zeta$ (which is $\eta$ for $x + 1$ neutrons) in terms of the same quantities for $\eta$. This recurrent scheme has been carried out for several values of the excitation energy $E_0$. Then the probability of emission of $x$ and only $x$ neutrons was obtained in the manner indicated above. The curves obtained, Fig. 10, show a striking similarity with the ($p$, $6n$) results. There is a slight displacement of the experimental maximum towards higher energies (remember also that the excitation energy is the kinetic energy) which is not very significant in view of the fact that the range-energy relation has not been gauged accurately. In fact, the lower value of the threshold obtained in the case of the ($d$, $7n$) reaction, where a more accurate comparison was done, may well indicate a small systematic error in the desired direction in the proton case.* Otherwise the general appearance *and in particular the width* of the curves are in fair agreement.

The excitation functions for the ($\alpha$, $p8n$) and ($\alpha$, $p5n$) reactions shown in Figs. 8 and 9 have very broad maxima as distinguished from the indicated sharp peaks and lower yields for the ($\alpha$, $6n$) and ($\alpha$, $7n$) excitation functions (the data for which were discussed in Section 3c3). There are two factors which contribute to this difference between the two types of reactions. First, in the ($\alpha$, $pxn$) reaction the potential barrier for the proton makes it necessary for the proton to carry with it more energy than an emitted neutron and therefore makes it possible to utilize extra energy to advantage. The second factor is connected with the complex nature of the helium ion, consisting of four nucleons with a possible uneven division of the kinetic energy between them at the time of impact. In the case of the ($\alpha$, $pxn$) reaction, only one proton from the helium ion need be retained by the struck nucleus. The ($\alpha$, $xn$ reaction demands a retention of two protons and hence a much closer approach to the formation of a compound nucleus.

The faster fall off in yield with increasing energy of the ($\alpha$, $p5n$) compared to the ($\alpha$, $p8n$) reaction is reasonable in view of the smaller energy requirement of the former. It is interesting to note that the excitation function for the ($p$, $\alpha 8n$) reaction shown in Fig. 4 presents a broad peak at a position toward the full energy of the incident proton. This is undoubtedly connected with the potential barrier for the outgoing alpha particle (or two protons), which can use relatively large amounts of energy to advantage.

It is unfortunate that the spread in energy of the bombarding particles is so great as to make it impossible to determine accurate threshold values for the various reactions. The rough result of about 40 MeV which was obtained for the ($d$, $7n$) reaction by comparison (see Fig. 7) with reactions of known threshold, determined with precision with low-energy-particle accelerators, indicates an average binding energy of about 7 to 7·5 MeV per neutron. This is a very reasonable value and can probably be used to estimate thresholds for ($d$, $xn$) and ($p$, $xn$) reactions in this region.

The excitation functions which have been determined in this work serve the very practical purpose of making it possible to estimate the optimum energy for the production of the maximum specific activity for isotopes produced by these and similar reactions. The results also suggest that in the case of ($p$, $xn$) and ($d$, $xn$) reactions, perhaps even when $x$ is as large as 10, the peaks are sufficiently sharp to make it possible to make isotopic assignments of new activities by measuring their excitation functions.

* See note on page 90

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## 5. EXPERIMENTAL DETAILS

### 184-*inch Cyclotron Beam Types*

With the Berkeley 184-inch cyclotron, there are three ways the charged particle beam can be used: as an internal beam, as an external beam, and as an electrostatically deflected beam. For use in the internal beam, a target can be inserted on a probe into the tank of the cyclotron to intercept the beam at any desired radius from about 20 inches up to the full radius of 81 inches. At present it is possible to obtain an internal beam current of about one microampere of deuterons or protons, and about 0·1 microampere of helium ions.

When the beam is brought out of the vacuum tank through thin aluminium windows and led into an external "cave," the external beam so produced has several advantages. Its energy definition is good (one-half to one per cent spread); it can be collimated to any desired shape and is very adaptable to experiments; it can be made to intercept the centre of a target foil; and it does not require that the target be in a vacuum, thus greatly increasing the number of bombardment possibilities. These advantages are obtained at the expense of a great sacrifice in beam current, which for the proton or deuteron beam is reduced to $10^{-5}$ to $10^{-4}$ microamperes. This, except in rare cases, is not enough to be very useful for chemical investigations of reactions with cross-sections of $10^{-2}$ barns or less.

Many of the advantages of the external beam are secured with a much less severe beam reduction by use of the electrostatically deflected beam.[14] This beam is produced by applying a pulsed voltage to a deflector electrode as the internal beam pulse reaches its maximum orbit of 81 inches. The particles are pushed in from their maximum orbit, and when they pass the end of the 120° arc of the deflector they again move in an orbit of radius close to 81 inches but with centre displaced so that the beam now intercepts the middle of a target at a distance from the centre of about 83 inches. The particles can be maximized on a certain portion of the target by adjusting the amount of voltage applied to the deflector. The reduction in intensity from that of the internal beam is a factor of 50 or more, but, in most of the reactions here studied, this could be tolerated.

### *Methods of Varying the Beam Energy; Calculations and Errors Involved*

A straightforward method of running excitation-function bombardments is to place the target probe at different radial positions in the full undeflected internal beam in successive bombardments. No absorbers are required and the beam energy is closely defined by the radius. The only energy spread is that of the incident beam, since no further energy spread or straggling is introduced by passage through a thick absorber stack. When the cross-section of the nuclear reaction being studied is low and/or the half-life or radiation characteristics of the product nucleus make it necessary to maximize the absolute yield of the product, the use of this method is clearly indicated. The principal objection lies in the difficulty of duplicating precisely the beam current and beam position in successive bombardments. To correct for these fluctuations, it is necessary to bombard with each target foil a monitor foil which undergoes some nuclear reaction for which an excitation function has previously been determined. Examples of useful monitor reactions are $C^{12}(d, n)N^{13}$, $Al^{27}(d, \alpha p)Na^{24}$, and $Al^{27}(p, 3pn)Na^{24}$. Polystyrene foils are commonly employed for the first reaction.

The stacked-foil technique has been used most frequently (see Appendix). Weighed target foils either alone or separated by intermediate absorber foils of aluminium or copper can be used to reduce the beam energy. A variation of this method is the bombardment of a thick target followed by the successive milling off of thin layers and the determination of the yield in each layer. This method in either variation is best performed with the deflected beam.

The range-energy relationships calculated by the Theoretical Physics Group at the University of California Radiation Laboratory were used in the present work to convert from absorber thickness to energy of the transmitted particles.[8] These data have been published in graphical form.[7]

The following values were taken for the maximum particle energies and the corresponding ranges in copper: 348-MeV protons, 97,250 mg/cm²; 194-MeV deuterons, 22,420 mg/cm²; and 388-MeV helium ions, 11,260 mg/cm². The total amount of absorber up to the middle of each foil was converted for convenience, to equivalent thickness (mg/cm²) of copper, and after subtraction from the full range value, the difference was used to determine the energy from the proper range-energy relationship.

[14] W. M. POWELL, L. R. HENRICH, Q. A. KERNS, D. C. SEWELL, and R. L. THORNTON *Rev. Sci. Instrum.* **19**, 506 (1948).

In this work the materials in the beam included copper, thorium, uranium, aluminium, and polystyrene foils. Range-energy relationships[7] were available for all three particles in copper and aluminium and for protons in carbon (from which that for deuterons in carbon could be calculated). It is assumed that carbon atoms alone are responsible for the stopping power of the polystyrene. In order to obtain values for thorium and uranium, the values given for lead were extrapolated by means of the relationship, $(Z/A)(\text{range}) = \text{constant}$. This extrapolation is sufficiently accurate for the present purpose, since the change in range is only about 2% between lead and thorium in terms of weight per unit area. Most of the beam-energy reduction occurred in the copper and the relatively smaller amounts of thorium or uranium were converted to copper equivalents by the following method. The copper equivalent, for example, of a certain amount of thorium was determined by calculating the ratio of the difference in range in thorium between the two energy values to that for copper and dividing the amount of thorium (mg/cm²) by this figure.

There are two major uncertainties involved in the use of the stacked-foil technique which tend to spread out a peak in an excitation-function experiment, particularly if the peak occurs at relatively low energies. First, there is the initial energy distribution of the beam. There is apparently an energy spread of up to 3% in the 184-inch cyclotron full-energy internal beam and electrostatically deflected beam, and of about 1% in the external beam. When protons of initial maximum energy 348 MeV are reduced to 50 MeV by copper absorbers, an initial spread of 1% in energy corresponds to a spread of about 15 MeV, and an initial 3% spread corresponds to about 50 MeV, at the 50-MeV level.

The other effect which contributes to the spreading out of the excitation-function peaks so as to give falsely large widths, is the straggling of the particle beams. Calculation of the extent of this is possible; a calculation indicating the straggling of 348-MeV protons introduced by passage through copper has been made by W. Aron, of the Theoretical Physics Group of the Radiation Laboratory. From his calculations it is seen that at 100 MeV the energy "width" due to straggling is about 4·3 MeV, while at 50 MeV it has increased to about 7·3 MeV. These figures represent root-mean-square deviations. In order to compare them with the above figures for the initial energy distribution, let us assume, for instance, that we have to do with a square distribution law, i.e. constant intensity within an interval of 3% width, and zero outside. The standard deviation in energy corresponding to this is $3(12)^{-1/2}\%$ or 0·87%. When protons of initial maximum energy 348 MeV are reduced to 50 MeV by copper absorbers, an initial deviation of 0·87% in energy corresponds to a final root-mean-square deviation in energy of 11·1 MeV, which is slightly larger than the effect of straggling at the 50-MeV level. It must be remembered, of course, that the initial energy spread of the beam can vary with the setting of the deflector, so that data obtained from one experiment cannot be applied directly to another experiment, even though conditions were very much the same.

These two effects lead to peaks which are appreciably wider than their true widths as illustrated by comparison of the results shown in Fig. 7 with those given for the same reactions as determined with machines which give low-energy particles directly.[12, 13] Another striking example of this comes from the work of E. L. Kelly, who used the value of 388 MeV for the most probable maximum energy of the helium-ion beam and roughly matched the peak energy on a $Bi^{209}(\alpha, 2n)At^{211}$ excitation curve taken through the use of aluminium absorbers with the electrostatically deflected beam of the 184-inch cyclotron[3] with a curve for the same reaction taken very carefully with the 39-MeV external helium-ion beam of the 60-inch Berkeley cyclotron.[15] In these experiments the width of the peak at half maximum for the electrostatically deflected beam determination was about 500 mg/cm² of aluminium compared to about 116 mg/cm² of aluminium on the 60-inch cyclotron.

It is clear that, since the effect of straggling can be estimated theoretically, and the relevant formulae are considered reliable, comparisons like those just made can be used to estimate, in a manner independent from other information, the energy spread of the initial beam. A very good example is the $C(d, n)$ reaction of Fig. 7. The excitation curve from low-energy machines plotted on a range scale would consist of a sharp peak of negligible width. The effect of straggling transforms this into a gaussian peak with a standard deviation of 150 mg/cm² of Al (this is the range straggling for reduction of a deuteron from 190 MeV to practically zero energy). The actually observed peak has a standard deviation about 3/2 of that obtained from straggling alone. Thus the effects of straggling and initial energy distribution are comparable in good agreement with the previous estimate.

Since the 348-MeV protons generated by the 184-inch cyclotron have a range of about 4·3 inches of copper, thick copper absorbers were required to decrease the beam energy between the thorium

[15] E. L. Kelly and E. Segrè *Phys. Rev.* **75**, 999 (1949).



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target foils. Because of this long range, an appreciable fraction of the beam in its progress through the stack is absorbed by producing nuclear reactions in the copper so that the beam is not only degraded in energy but is also attenuated. Rough correction factors for this effect were obtained from measurements made by V. PETERSON of the Radiation Laboratory, who measured the amount of absorption of the proton beam in copper blocks of known thickness. A plot of the data, absorber thickness vs. transmission, shows an exponential dependence for the experimental arrangement used, with a transmission of about 0·6 for 70 g/cm² copper absorber, the data being good to about 20%. A correction for this nuclear absorption has been applied to the yield calculations for all of the samples from proton bombardments. No corrections were made in the case of the deuteron and helium-ion bombardments, where the ranges are so much less as to make the error introduced smaller.

No scattering corrections were applied to any of the bombardments. In all cases these corrections would have a relatively minor effect on the general shape of the excitation function compared to the corrections due to initial beam distribution, straggling, etc.

### *Experimental Details in Use of the Three Beam Types*

1. *Internal beam bombardments.* The small amount of $U^{230}$ and $U^{229}$ alpha activity produced by the $Th^{232}(\alpha, 6n)$ and $Th^{232}(\alpha, 7n)$ reactions made it necessary to use the internal beam for the determination of their excitation functions. Thin foils were mounted on the probe and the beam energy determined by an accurate determination of the radius to the leading edge of the foil. The target thickness in each case was only a few per cent of the total range of the incident particles.

Attempts were made to use the stacked-foil technique in the internal beam, but the runs were unsatisfactory, since the variation of the angle of incidence of the internal beam served to spread out and falsify the peaks of the excitation functions studied.

2. *External beam measurements.* The reaction cross-sections and product-isotope decay characteristics were not favourable enough in the reactions studied here to permit use of the external beam except for absolute-yield determinations in the two most favourable cases. These two were the reactions $Th^{232}(p, 6n)Pa^{227}$ and $Th^{232}(d, 7n)Pa^{227}$. Even here only a few thousand disintegrations of $Pa^{227}$ per minute at shutdown were obtained from 40-min bombardments of 5-mil thorium at full energy. In these experiments the current passing through the target was collected and measured in a Faraday cup.

3. *Electrostatically deflected beam experiments.* Most of the experiments were run in the electrostatically deflected beam with the use of the apparatus shown in Fig. 11. In this apparatus, accurately weighed copper absorbers of various thicknesses with sides milled parallel to within 0·2 mils were employed to reduce the beam energy. As much as 4·3 inches of copper could be inserted to ensure complete stoppage of the most energetic beam (348-MeV protons). The 5-mil target material in the form of ¾-inch-diameter metal disks was fastened by small pieces of scotch tape (½ inch to ⅛ inch) to masks of 5-mil copper, and thus located ¾ of an inch from the beam-side edge and midway between top and bottom of the copper absorbers. The copper on the beam side of the target material serves the very important function of reducing the background due to particles coming in from the side of the absorber stack to about one hundredth (or less in some cases) of the maximum activity of the excitation curve. A support ledge is provided on the beam side of the absorber stack to permit the addition of more absorber if it should become necessary to reduce this background further.

The 1½-inch-thick copper collimator with the ¾-inch collimating hole was used in front of the absorber stack to increase the definition in the deuteron and helium-ion bombardments. It was possible to obtain reproducibly good results without it, as shown by the proton bombardments, in which it could not be used for lack of space. The use of the collimator, where possible, actually increased the yields of activity by a factor of 20 or more; this results from the fact that the collimator, being grounded, allows the beam current to be maximized on the target foils themselves, rather than to strike haphazardly on the block of absorbers, which ensures that the target foils are hit by the "hot spot" of the beam. Errors due to scattering could have been corrected by making the diameter of the sample disks about 1½ times greater than the diameter of the collimating hole. This would have introduced more target material into the chemical procedure and slowed it down if the present collimator had been used. If smaller collimators had been used, less beam would have hit the target. In either case the final yield of the product would have been considerably reduced, and hence it was decided to neglect the small scattering correction.

Other details of the apparatus are designed to ensure the absorbers in the stack being held rigidly in place.

When the apparatus is assembled, the copper current-reading contact rests upon the absorber stack, which is insulated from the rest of the apparatus both by the "Dilectine" insulator tray and by pieces of mica between the stack and the absorber shield which is grounded to the absorber support.

EXCITATION FUNCTION APPARATUS

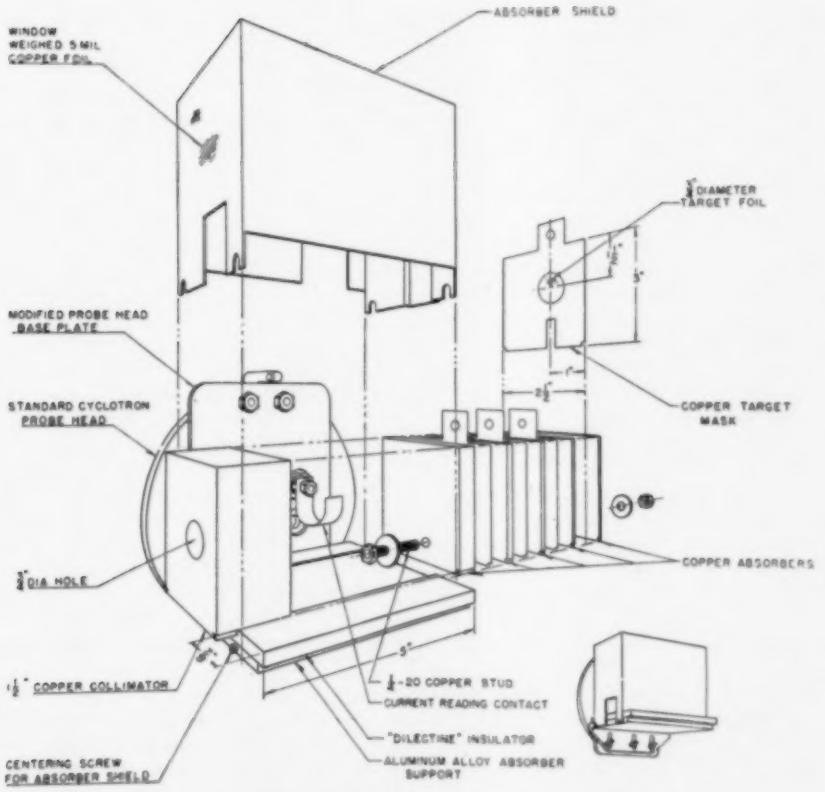


FIG. 11—Excitation-function apparatus.

It is necessary to shield the absorber stack electrically from the external electrostatic fields which would influence the current readings, and the copper box is used for this purpose. This absorber shield is kept in position by two screws on each end of the absorber support. The beam passes through a thin copper-foil window in the shield, this window thickness being included in the range-energy calculations. The entire apparatus fits onto the standard cyclotron probe head.

Immediately after bombardment, the four centering screws are loosened, the absorber shield removed (with a pair of tongs by a small hook which is not shown on the drawing), the bolt on the absorber stack loosened, a small rod slipped through the tab holes in the masks, and the masks lifted free. The target disks are removed from the masks in the chemical laboratory and subjected to the chemical operations described below.

To maximize the beam on the target, it is possible to vary both the radius of the target apparatus

and the voltage on the deflector. Furthermore, the entire tray of absorbers can be raised or lowered to position the targets vertically in the beam by loosening the wing nuts holding the absorber support, as shown in the insert in the drawing.

With this apparatus and suitable absorbers, it is possible to determine simultaneously as many as sixteen points on an excitation curve (with a minimum interval of 5 MeV between points for alpha bombardments and much less for deuteron and proton bombardments).

### *Chemical Procedures for Protactinium and Uranium Separation*

The only essential requirement of the chemical procedure is that the amount of interfering radioactivity be reduced quickly to such a degree that the product isotopes of interest can be accurately measured through some characteristic radiation (in the present case by the alpha-particles of characteristic energy and half-life). However, these are severe requirements when it is considered that (1) an exceedingly complex mixture of radioactivities is produced; (2) up to sixteen samples must be processed and counted before the short-lived activities (such as the 38·3-min $Pa^{227}$) have disappeared; (3) the chemical yields must be reproducible; (4) the final samples must be virtually weightless to permit accurate determination of the alpha-particle energy spectrum.

The following separation procedure based on the solvent extraction of an organic complex ion of the element fulfilled the above conditions for protactinium. STUDIER, HAGEMANN, HYDE,[16] and others were the first to apply to bombardment chemistry the fact that protactinium forms a complex with the $\beta$-diketone thenoyltrifluoroacetone[9] (TTA), which is soluble in benzene and other organic solvents and may be extracted from a strongly acidic aqueous solution. Many other elements form solvent extractable TTA complexes, but no other alpha-particle-emitting element except protactinium will extract from strongly acidic solution.

In the chemical procedure[17] each thorium (~0·4 g) or uranium (~0·7 g) disk was dissolved in a 125-ml Phillips beaker with 10 ml concentrated nitric acid and, in the case of thorium, one drop of 0·2 M ammonium fluosilicate solution. The solution was heated gently on a hot plate until the reaction started. The solution was diluted with 10 ml of water and transferred into a separatory funnel (consisting of a 40-ml calibrated centrifuge cone with a stopcock sealed to the bottom). 10 ml of 0·4 M thenoyltrifluoroacetone (TTA) in benzene solution was added and the mixture stirred for five minutes. The aqueous and organic layers for each sample were collected in separate tubes and about half of the organic layer (containing the protactinium) evaporated on a platinum disk, ignited to destroy the organic matter and form a weightless film, and counted for gross alpha-disintegration rate. The evaporations were made carefully to prevent loss of protactinium. This was especially necessary in the case of the uranium bombardments. One-fourth-inch washers were used to raise the platinum disks above the surface of the hot plate and thus allow loading of as much as 1 ml of the benzene solution at a time. It has been possible to start counting the samples from a run of sixteen foils as early as 110 min after the end of bombardment. This protactinium procedure worked smoothly when applied to thorium targets, but somewhat erratically, although still for the most part consistently when applied to uranium targets.

The chemical yields of the runs reported in this paper are consistent among themselves to within 5 to 10%, but the absolute chemical yield has in most cases been left undetermined. It is known that the majority of the protactinium is extracted in the one equilibration with TTA-benzene solution.

The absolute cross-sections for the reactions $Th^{232}(p, 6n)Pa^{227}$ and $Th^{232}(d, 7n)Pa^{227}$ were determined for runs made with the external beam, as mentioned previously. In these runs the chemical yield of protactinium was determined with the use of $Pa^{231}$ tracer. Precautions were taken to eliminate the uncertainties frequently encountered in the exchange of $Pa^{231}$ tracer because of unknown ionic or colloidal species formed on standing in aqueous solutions particularly of low acidity, but it is not certain that this was accomplished successfully. Therefore, the absolute yields reported are subject to some question.

The efforts to develop a uranium purification procedure for the $Th(\alpha, xn)U$ studies were not very satisfactory. An ether-extraction procedure of the type described by NEWTON[18] suggested itself as a very promising starting-point, but in attempting to reduce this to a minimum-step procedure suitable for the simultaneous processing of sixteen samples with enough speed to detect a one-hour

[16] M. H. STUDIER, F. HAGEMANN JR., and E. K. HYDE. Unpublished work (1945).
[17] W. W. MEINKE, U.S. Atomic Energy Commission Declassified Documents AECD-2738 (Aug., 1949) and AECD-2750 (July-Aug., 1949).
[18] A. S. NEWTON *Phys. Rev.* **75**, 209 (1949).

half-life, difficulties developed. Some success in removing all extraneous activities from a uranium fraction was attained with a more lengthy procedure similar to that devised by CRANE.[17] It involves precipitation of the uranium on lanthanum hydroxide, followed by dissolution and removal of impurities by zirconium iodate precipitations from the uranyl solution, in addition to the ether extractions. The yield has been found to be rather low (less than 10%), unless extra time is spent in increasing it by re-extractions and reprecipitations.

### *Counting and Pulse-analysis Measurements*

The alpha-particle emission rate of the samples was determined in an ordinary argon ionization chamber in which 50–52% of the particles are detected. A standard scale of 512-scaling circuit was used and the measured counting rates were such that coincidence corrections were not necessary. The decay of the emission rate was followed to identify the half-life in question. Appropriate allowance was made for the contribution of daughters to the gross activities in calculating the true counting rate of the parent itself.

In many cases it was necessary to subject the samples to alpha-pulse analysis with the 48-channel differential pulse analyser.[10] Pulse analysis was especially important in determining the amount of beta-particle-emitting $Pa^{230}$ by measurement of the amount of the alpha-emitting $U^{230}$ daughter present several weeks after bombardment. The amount of $Pa^{230}$ initially present was calculated by means of the appropriate daughter-growth equation and decay constants,[19] allowing for the 10% branching decay of $Pa^{230}$ by negative beta-particle emission reported by STUDIER and BRUEHLMAN.[11]

In the experiments in which the beta-particle emission rate of the polystyrene and aluminium targets were measured, an end-window, bell-type Geiger tube filled with a 9-cm argon and 1-cm ethyl-alcohol gas mixture was employed. The thickness of the mica window was 3 mg/cm². Samples were placed 7·0 cm below the counter window, where a geometrical counting yield of 1·7% obtains. A scale of 64-scaling circuit was used and a coincidence correction of 1·2% per thousand pulses per minute was applied to all counting rates.

All of the alpha-disintegration rates plotted in the graphs have been corrected for decay back to the end of bombardment, and refer to the isotope in question (i.e. the gross counting rates have been corrected for activity due to the daughter isotopes). The relative yields were normalized to 0·4 g thorium, 0·7 g uranium, 0·1 g aluminium, or 0·04 g polystyrene. In those cases where more than one run on a certain reaction was made, the one that was considered most accurate or more consistent was taken as a standard and the yields of the other runs normalized to it. In one of the runs on the $Th^{232}$ $(d, 7n)$ reaction, a mistake was apparently made in tabulating the absorbers, in which one absorber was overlooked, and the results without correction gave a plot with the peak shifted about 12 MeV. In this case the error in tabulation was assumed and the corresponding correction was made in plotting the data in Fig. 5.

*Acknowledgements*—We wish to thank JAMES T. VALE and the crew of the 184-inch cyclotron for their assistance in carrying out this work. It is a pleasure to acknowledge the interest of Professors E. M. MCMILLAN and I. PERLMAN, and of EARL K. HYDE and ALBERT GHIORSO in this problem. We should also like to express our appreciation to HERMAN P. ROBINSON for his help in the design and procurement of equipment; and to W. A. ARON, B. G. HOFFMAN, and F. C. WILLIAMS, and to V. PETERSON for permission to include material not published elsewhere.

[19] M. H. STUDIER and E. K. HYDE *Phys. Rev.* **74**, 591 (1948).

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## APPENDIX*

*Bibliography of Thin-target Excitation Functions for Charged-particle Reactions*

### DEUTERONS

*1·9 MeV:*

$Na^{23}(d, p)Na^{24}$—E. O. LAWRENCE *Phys. Rev.* **47,** 17 (1935).

$Al^{27}(d, p)Al^{28}$—E. M. MCMILLAN and E. O. LAWRENCE *Phys. Rev.* **47,** 343 (1935).
(Historically the first use of the stacked-foil technique with accelerated particles.)

*2·8 MeV:*

$C^{13}(d, n)N^{13}$—C. L. BAILEY, M. PHILLIPS, and J. H. WILLIAMS *Phys. Rev.* **62,** 80 (1942).

*3·5 MeV:*

$Mg^{26}(d, p)Mg^{27}$; $Mg^{26}(d, \alpha)Na^{24}$—M. C. HENDERSON *Phys. Rev.* **48,** 855 (1935).

$Na^{23}(d, p)Na^{24}$; $Al^{27}(d, p)Al^{28}$; $Si^{29}(d, p)Si^{31}$; $Cu^{63}(d, p)Cu^{64}$—E. O. LAWRENCE, E. M. MCMILLAN, and R. L. THORNTON *Phys. Rev.* **48,** 493 (1935).

$C^{12}(d, n)N^{13}$; $N^{14}(d, n)O^{15}$; $O^{16}(d, n)F^{17}$—H. W. NEWSON *Phys. Rev.* **48,** 790 (1935).

*5 MeV:*

$C^{13}(d, n)N^{13}$; $N^{14}(d, n)O^{15}$; $O^{16}(d, n)F^{17}$—H. W. NEWSON *Phys. Rev.* **51,** 620 (1937).

$A^{40}(d, p)A^{41}$—A. H. SNELL *Phys. Rev.* **49,** 555 (1936).

$Ni^{60}(d, n)Cu^{61}$—R. L. THORNTON *Phys. Rev.* **51,** 893 (1937).

$Cu^{63}(d, p)Cu^{64}$—S. N. VAN VOORHIS *Phys. Rev.* **50,** 895 (1936).

*6 MeV:*

$Pd^{108}(d, p)Pd^{109}$; $Pd^{110}(d, n)Ag^{111}$—J. D. KRAUS and J. M. CORK *Phys. Rev.* **52,** 763 (1937).

$Al^{27}(d, p)Al^{28}$; $Si^{29}(d, p)Si^{31}$—W. RIEZLER *Naturwiss.* **34,** 157 (1947).

*9 MeV:*

$Fe^{54}(d, n)Co^{55}$—J. M. CORK and B. R. CURTIS *Phys. Rev.* **55,** 1264 (1939).

$Pb^{206}(d, 2n)Bi^{206}$; $Pb^{208}(d, p)Pb^{209}$—K. FAJANS and A. F. VOIGT *Phys. Rev.* **60,** 619 (1941).

$U^{238}(d, p)U^{239}$—N. FEATHER and R. S. KRISHNAN *Proc. Camb. Phil. Soc.* **43,** 267 (1947).

$Th^{232}(d, \text{fiss})$; $U^{238}(d, \text{fiss})$—D. H. T. GANT and R. S. KRISHNAN *Proc. Roy. Soc.* **A178,** 474 (1941).

$Bi^{209}(d, n)Po^{210}$; $Bi^{209}(d, p)Bi^{210}$—D. G. HURST, R. LATHAM, and W. B. LEWIS *Proc. Roy. Soc.* **A174,** 126 (1940).

$Th^{232}(d, \text{fiss})$; $U^{238}(d, \text{fiss})$—I. C. JACOBSEN and N. O. LASSEN *Phys. Rev.* **58,** 867 (1940).

$Ag^{107}(d, p2n)Ag^{106}$—R. S. KRISHNAN and T. E. BANKS *Nature* **145,** 777 (1940).

$F^{19}(d, H^3)F^{18}$—R. S. KRISHNAN *Nature* **148,** 407 (1941).

$Ag^{107}(d, p)Ag^{108}$; $Ag^{107}(d, H^2)Ag^{106}$; $Ag^{107}(d, 2n)Cd^{107}$; $Ag^{109}(d, 2n)Cd^{109}$—R. S. KRISHNAN *Proc. Camb. Phil. Soc.* **36,** 500 (1940).

$Au^{197}(d, p)Au^{198}$; $Au^{197}(d, 2n)Hg^{197}$—R. S. KRISHNAN *Proc. Camb. Phil. Soc.* **37,** 186 (1941).

$Cu^{63}(d, p)Cu^{64}$; $Cu^{63}(d, H^3)Cu^{62}$; $Sb^{121}(d, p)Sb^{122}$; $Sb^{121}(d, H^3)Sb^{120}$—R. S. KRISHNAN and T. E. BANKS *Proc. Camb. Phil. Soc.* **37,** 317 (1941).

$Pt^{196}(d, p)Pt^{197}$; $Pt^{198}(d, p)Pt^{199}$—R. S. KRISHNAN and E. A. NAHUM *Proc. Camb. Phil. Soc.* **37,** 422 (1941).

$Au^{197}(d, p)Au^{198}$; $Au^{197}(d, 2n)Hg^{197}$; $Tl^{205}(d, p)Tl^{206}$; $Tl^{205}(d, 2n)Pb^{205}$; $Pb^{208}(d, p)Pb^{209}$; $Bi^{209}(d, p)Bi^{210}$; $Bi^{209}(d, n)Po^{210}$; $Th^{232}(d, p)Th^{233}$—R. S. KRISHNAN and E. A. NAHUM *Proc. Roy. Soc.* **A180,** 333 (1942).

$Bi^{209}(d, p)Bi^{210}$; $Bi^{209}(d, n)Po^{210}$—H. E. TATEL and J. M. CORK *Phys. Rev.* **71,** 159 (1947).

* *Note added January* 1956. In this appendix there is presented a relatively complete compilation of charged-particle excitation functions found in the literature up to 1950. Since that time the number of papers reporting data of this sort have increased considerably. In September 1955 this compilation was brought up to date for bombarding energies above 2 MeV by O. U. ANDERS and W. W. MEINKE. Photocopies of the excitation-function curves were made and pasted on punch cards, which were then categorized according to element bombarded, element produced, etc. A microfilm has been made of the 500 odd cards in this file and has been deposited with the American Documentation Institute, c/o Library of Congress, Washington 25, D.C., U.S.A., for distribution at a nominal cost.

10 *MeV:*

$Bi^{209}(d, p)Bi^{210}$; $Bi^{209}(d, n)Po^{210}$—J. M. CORK, J. HALPERN, and H. TATEL *Phys. Rev.* **57,** 371 (1940).
$Fe^{54}(d, n)Co^{55}$; $Fe^{54}(d, \alpha)Mn^{52}$—J. M. CORK and J. HALPERN *Phys. Rev.* **57,** 667 (1940).
$Ag^{107}(d, 2n)Cd^{107}$—D. N. KUNDU and M. L. POOL *Bull. Amer. Phys. Soc.* **25,** No. 4, 11 (1950). (Abstract).

11 *MeV:*

$Be^{9}(d, p)Be^{10}$—E. M. MCMILLAN *Phys. Rev.* **72,** 591 (1947).

14 *MeV:*

$Na^{23}(d, p)Na^{24}$; $Br^{81}(d, p)Br^{82}$; $Br^{79}(d, 2n)Kr^{79}$—E. T. CLARKE and J. W. IRVINE, Jr. *Phys. Rev.* **66,** 231 (1944).
$Mg^{24}(d, \alpha)Na^{22}$; $Mg^{26}(d, \alpha)Na^{24}$; $Cu^{65}(d, p)Cu^{64}$; $Cu^{65}(d, \alpha)Ni^{63}$; $Cu^{63}(d, 2n)Zn^{63}$; $Cu^{65}(d, 2n)Zn^{65}$—E. T. CLARKE and J. W. IRVINE, Jr. *Phys. Rev.* **69,** 680 (1946).
$Al^{27}(d, p\alpha)Na^{24}$—E. T. CLARKE *Phys. Rev.* **71,** 187 (1947).

15 *MeV*:

$Bi^{209}(d, p)Bi^{210}$; $Bi^{209}(d, n)Po^{210}$—J. M. CORK *Phys. Rev.* **70,** 563 (1946).
$Cu^{63}(d, p)Cu^{64}$; $Cu^{63}(d, 2n)Zn^{63}$—R. S. LIVINGSTON and B. T. WRIGHT *Phys. Rev.* **58,** 656 (1940).
$Ta^{181}(d, p)Ta^{182}$—KUAN-HAN SUN, F. A. PECJAK, R. A. CHARPIE, J. F. NECHAJ, *Phys. Rev.* **78,** 338 (1950).

19 *MeV:*

$Bi^{209}(d, p)$RaE; $Bi^{209}(d, n)Po^{210}$; $Bi^{209}(d, 3n)Po^{206}$—E. L. KELLY and E. SEGRÈ, *Phys. Rev.* **75,** 999 (1949).
$Th^{232}(d,$ fiss); $U^{238}(d,$ fiss)—J. JUNGERMAN and S. C. WRIGHT *Phys. Rev.* **74,** 150 (1948).

190 *MeV*:

$Al^{27}(d, \alpha p)Na^{24}$; $Al^{27}(d, \alpha p2n)Na^{22}$—A. C. HELMHOLZ and J. M. PETERSON, *Phys. Rev.* **73,** 541 (1948). (Abstract).
$Cu^{63, 65}(d, )Zn^{63}$; $Cu^{63, 65}(d, )Zn^{62}$; $Cu^{63, 65}(d, )Ni$; $Cu^{63, 65}(d, )Co$—D. BOCKHOP, A. C. HELMHOLZ, and J. M. PETERSON *Phys. Rev.* **74,** 1559 (1948). (Abstract).
$Cu^{63, 65}(d, )Mn^{52}$; $Cu^{63, 65}(d )Mn^{54}$; $Cu^{63, 65}(d )Fe^{59}$; $Cu^{63, 65}(d, )Co^{56}$; $Cu^{63, 65}(d, )Zn^{62}$; $Cu^{63, 65}(d, )Zn^{63}$; $Cu^{63, 65}(d, )Cu^{64}$—D. BOCKHOP, A. C. HELMHOLZ, S. D. SOFTKY, J. W. ROSE, and T. BREAKEY *Phys. Rev.* **75,** 1469 (1949). (Abstract).
$Cu^{63, 65}(d, )Mn^{52}$; $Cu^{63, 65}(d, )Mn^{54}$; $Cu^{63, 65}(d, )Fe^{52}$; $Cu^{63, 65}(d, )Fe^{59}$; $Cu^{63, 65}(d, )Ni^{57}$; $Cu^{65}(d, 2p)Ni^{65}$; $Cu^{63, 65}(d, )Cu^{61}$; $Cu^{63, 65}(d, )Cu^{64}$; $Cu^{63, 65}(d, )Zn^{63}$; $Cu^{63, 65}(d, )Zn^{62}$—F. O. BARTELL, A. C. HELMHOLZ, S. D. SOFTKY, D. B. STEWART, University of California Radiation Laboratory Unclassified Report UCRL-757 (July, 1950).

195 *MeV:*

$C^{12}(d, dn)C^{11}$—R. L. THORNTON and R. W. SENSEMAN *Phys. Rev.* **72,** 872 (1947).

## HELIUM IONS

5·3 *MeV:*

$F^{19}(\alpha, p)Ne^{22}$; $F^{19}(\alpha, n)Na^{22}$—N. K. SAHA *Z. Phys.* **110,** 473 (1938).
$Al^{27}(\alpha, n)P^{30}$—A. SZALAY *Nature* **141,** 972 (1938).
$Al^{27}(\alpha, n)P^{30}$—A. SZALAY *Z. Phys.* **112,** 29 (1939).

6 *MeV:*

$C^{13}(\alpha, n)N^{16}$—W. RIEZLER *Naturwiss.* **34,** 157 (1947).

7 *MeV:*

$Na^{23}(\alpha, n)Al^{26}$; $P^{31}(\alpha, n)Cl^{34}$—H. BRANDT *Z. Phys.* **108,** 726 (1938).

9 *MeV:*

$Li^{7}(\alpha, n)B^{10}$—O. HAXEL and E. STUHLINGER *Z. Phys.* **114,** 178 (1939).
$B(\alpha, n)N$; $Be^{9}(\alpha, n)C^{12}$—E. STUHLINGER *Z. Phys.* **114,** 185 (1939).

11 *MeV:*

$Cu^{63}(\alpha, n)Ga^{66}$; $Cu^{65}(\alpha, n)Ga^{68}$—W. B. MANN *Phys. Rev.* **52,** 405 (1937).

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20 *MeV:*

$Rh^{103}(\alpha, n)Ag^{106}$(25m); $Rh^{103}(\alpha, n)Ag^{106}$(8·2d); $Rh^{102}(\alpha, 2n)Ag^{105}$—H. L. BRADT and D. J. TENDAM *Phys. Rev.* **72,** 1117 (1947).

$Ag^{109}(\alpha, n)In^{112}$; $Ag^{109}(\alpha, 2n)In^{111}$—D. J. TENDAM and H. L. BRADT *Phys. Rev.* **72,** 1118 (1947).

32 *MeV:*

$Bi^{209}(\alpha, 2n)At^{211}$—D. R. CORSON, K. R. MACKENZIE, and E. SEGRÈ *Phys. Rev.* **58,** 672 (1940).

37 *MeV:*

$In^{115}(\alpha, n)Sb^{118}$; $In^{115}(\alpha, 2n)Sb^{117}$; $In^{115}(\alpha, 3n)Sb^{116}$—G. M. TEMMER *Phys. Rev.* **76,** 424, 1002 (1949).

38 *MeV:*

$Bi^{209}(\alpha, 2n)At^{211}$; $Bi^{209}(\alpha, 3n)At^{210}$—E. L. KELLY and E. SEGRÈ *Phys. Rev.* **75,** 999 (1949).

$Th^{232}(\alpha$, fiss); $U^{238}(\alpha$, fiss)—J. JUNGERMAN and S. C. WRIGHT *Phys. Rev.* **74,** 150 (1948).

$Ag^{107}(\alpha, n)In^{110}$; $Ag^{107}(\alpha, 2n)In^{109}$; $Ag^{109}(\alpha, 2n)In^{111}$; $Ag^{109}(\alpha, 3n)In^{110}$—S. N. GHOSHAL *Phys. Rev.* **73,** 417 (1948).

$Ni^{60}(\alpha, n)Zn^{63}$; $Ni^{60}(\alpha, 2n)Zn^{62}$; $Ni^{60}(\alpha, pn)Cu^{62}$; $Ag^{107}(\alpha, n)In^{110}$; $Ag^{107}(\alpha, 2n)In^{109}$; $Ag^{107}(\alpha, 3n)In^{108}$; $Ag^{109}(\alpha, 2n)In^{111}$; $Ag^{109}(\alpha, 3n)In^{110}$—S. N. GHOSHAL *University of California Radiation Laboratory Unclassified Report UCRL-*709. Revised (July 1950).

380 *MeV:*

$Al^{27}(\alpha, \alpha 2pn)Na^{24}$; $Al^{27}(\alpha, 2\alpha n)Na^{22}$—A. C. HELMHOLZ and J. M. PETERSON *Phys. Rev.* **73,** 541 (1948)

390 *MeV:*

$C^{12}(\alpha, \alpha n)C^{11}$—R. L. THORNTON and R. W. SENSEMAN *Phys. Rev.* **72,** 872 (1947).

## PROTONS

4 *MeV:*

$O^{18}(p, n)F^{18}$—L. A. DUBRIDGE, S. W. BARNES, J. H. BUCK, and C. V. STRAIN *Phys. Rev.* **53,** 447 (1938).

5 *MeV:*

$Ag^{107}(p, n)Cd^{107}$—D. N. KUNDU and M. L. POOL *Bull. Amer. Phys. Soc.* **25,** No. 4, 11 (1950). (Abstract).

5·7 *MeV:*

$N^{14}(p, \alpha)C^{11}$—W. H. BARKAS *Phys. Rev.* **56,** 287 (1939).

6·6 *MeV:*

$Cr^{52}(p, n)Mn^{52}$—A. HEMMENDINGER *Phys. Rev.* **58,** 929 (1940).

7 *MeV:*

$Pd^{106}(p, n)Ag^{106}$; $Pd(p, n)Ag(8d + 45d)$—T. ENNS *Phys. Rev.* **56,** 872 (1939).

$Ni^{61}(p, n)Cu^{61}$; $Ni^{64}(p, n)Cu^{64}$; $Cu^{63}(p, n)Zn^{63}$; $Zn^{68}(p, n)Ga^{68}$; $Pd^{106}(p, n)Ag^{106}$; $Ag^{107}(p, n)Cd^{107}$; $Cd^{114}(p, n)In^{114}$—V. F. WEISSKOPF and D. H. EWING *Phys. Rev.* **57,** 472 (1940).

16 *MeV:*

$Cu^{65}(p, pn)Cu^{64}$—J. R. RICHARDSON and B. T. WRIGHT *Phys. Rev.* **70,** 445 (1946).

32 *MeV:*

$Cu^{63}(p, n)Zn^{63}$; $Cu^{63}(p, 2n)Zn^{62}$; $Cu^{63}(p, pn)Cu^{62}$—S. N. GHOSHAL *University of California Radiation Laboratory Unclassified Report UCRL-*709 Revised (July, 1950).

140 *MeV:*

Boric acid $(p, \ )C^{11}$; $C^{12}(p, pn)C^{11}$—W. W. CHUPP and E. M. MCMILLAN *Phys. Rev.* **72,** 873 (1947).

350 *MeV:*

$C^{12}(p, pn)C^{11}$—LEE AAMODT, VINCENT PETERSON, and ROBERT PHILLIPS *Phys. Rev.* **78,** 87 (1950). (Abstract).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 93 to 103. Pergamon Press Ltd., London

# RADIATIONS OF AMERICIUM-246*

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(*Received* 23 *February* 1956)

**Abstract**—The beta spectra of an equilibrium sample of $Pu^{246}$-$Am^{246}$ were examined with a magnetic-lens beta-ray spectrometer and a scintillation spectrometer. The $Pu^{246}$-$Am^{246}$ equilibrium sample and samples of $Am^{246}$ were investigated with gamma-ray scintillation spectrometers. Coincidence studies of the radiations were also performed.

The data indicate that the decay of $Am^{246}$ is extremely complex, involving five beta-ray groups and many gamma rays. On the basis of gamma-beta coincidence measurements, the disintegration energy is 2·41 ± 0·10 MeV.

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## 1. INTRODUCTION

THE decay chain $Pu^{246} \xrightarrow{10\cdot85\ \text{day}}_{\beta^-} Am^{246} \xrightarrow{25\ \text{min}}_{\beta^-} Cm^{246}$ (2300 yr)[1] has previously been identified and preliminary investigations of the radiations have been made.[2] However, since additional samples of these nuclides have recently been obtained, further investigations of the $Am^{246}$ radiations and decay scheme have been made. A magnetic-lens beta-ray spectrometer and beta-ray and gamma-ray crystal spectrometers in conjunction with coincidence techniques were utilized.

## 2. CHEMICAL PROCEDURE

It was necessary to devise a procedure which would separate plutonium (from which the americium could then be "milked") from the other very heavy elements present, and furnish a decontamination factor of about $10^{10}$ from the fission products which constitute the majority of the activity resulting from neutron irradiation of transthorium elements. The following procedure, by taking advantage of the different chemical properties of the 3+, 4+, and 6+ valence states of plutonium,[3] appears to be nearly specific for plutonium and provides a decontamination factor from fission products of at least $10^5$ per cycle.

Solution of the original sample was attained by treatments with nitric, perchloric, and hydrochloric acids; the final solution in most cases was 4 N in HCl. In order to reduce this rather large volume of solution, lanthanum carrier was added and the solution was made alkaline with $NH_4OH$ to precipitate $La(OH)_3$. The precipitate was centrifuged, washed, dissolved, and reprecipitated. Finally, the precipitate was dissolved in concentrated HCl containing $HNO_3$ (100 $\lambda$ of $HNO_3$ per 15 ml of HCl) and passed through a Dowex-1(X10) anion-exchange resin column which had been equilibrated with a similar HCl-$HNO_3$ solution. The resin had been previously

* This work was done under the auspices of the U.S. Atomic Energy Commision.

[1] C. I. BROWNE, D. C. HOFFMAN, W. T. CRANE, J. P. BALAGNA, G. H. HIGGINS, J. W. BARNES, R. W. HOFF, H. L. SMITH, J. P. MIZE, and M. E. BUNKER *J. Inorg. Nucl. Chem.* **1**, 254 (1955).

[2] D. ENGELKEMEIR, P. R. FIELDS, S. FRIED, G. L. PYLE, C. M. STEVENS, L. B. ASPREY, C. I. BROWNE, H. L. SMITH, and R. W. SPENCE *J. Inorg. Nucl. Chem.* **1**, 345 (1955).

[3] *The Transuranium Elements* National Nuclear Energy Series, IV-14B, Papers 1.6 and 3.2.

washed with HCl and water, graded, and kept as a water slurry until used. After repeated washings with the HCl-$HNO_3$ solution to remove the transplutonics and rare earths, the plutonium was eluted with a 0·25 M HI solution which had been saturated with HCl gas. After destroying the HI in the eluate, further purification of the plutonium was obtained by three to four cycles of the following chemistry. The plutonium was oxidized with $KMnO_4$, a byproduct $LaF_3$ was precipitated, and the plutonium in the centrifugate was reduced with $NH_2OH{\cdot}HCl$ and reprecipitated with $LaF_3$. The precipitate was then dissolved in $H_3BO_3$ and concentrated HCl, passed through a Dowex-1 resin column, and eluted with an HI-HCl solution as before. Decontamination was considered satisfactory when the ratio of $\beta/\alpha$ activity of successive samples removed during the purification remained nearly constant. In the last cycle, the plutonium was left on the column so that the 25-min $Am^{246}$ activity could be "milked" from the column as desired. This was done at times such that the $Pu^{245} \xrightarrow[\beta^-]{12\ hr} Am^{245} \xrightarrow[\beta^-]{2{\cdot}08\ hr} Cm^{245}$ had decayed and would not interfere in the examination of the $Am^{246}$ radiations.

Later the plutonium was eluted, and a $Pu^{246}$-$Am^{246}$ equilibrium sample was prepared by evaporating the final eluate to dryness, dissolving it in dilute HCl, and evaporating it to dryness on a rubber hydrochloride film. The final dried sample had a diameter of 3/16 in.

## 3. SINGLES SPECTRA

*Beta Radiation*

A study of the equilibrium sample of $Pu^{246}$-$Am^{246}$ was made with a magnetic-lens beta-ray spectrometer. The spectrum is shown in Fig. 1. Conversion lines were observed at 51, 65, 74, 94, 114, 127, and 156 keV. The lines at 51 and 156 keV correspond to the $K$ and $L$ lines of a 178 keV gamma transition in the decay of $Pu^{246}$ ($51 + 124{\cdot}9 = 176$; $156 + 22{\cdot}9 = 179$). The $K/L$ ratio is $\sim$5, which indicates an $M1 + E2$ transition. (Extrapolation of ROSE's[4] tables of $K$ and $L$ conversion coefficients gives 6·3 as the $K/L$ ratio for an $M1$ transition and 0·2 for an $E2$ transition at 178 keV and $Z = 95$.) This transition appears to be associated principally with the decay of $Pu^{246}$, since the gamma spectra of the equilibrium sample show a gamma ray of approximately 175 keV, while the "milked" $Am^{246}$ shows little or none. If one assumes that the remaining observed lines are $L$ lines with no $K$ conversion electron lines or whose associated $K$ lines are at energies which are too low to be observed because of the detector-window thickness, then gamma energies of 89, 97, 118, 138, and 150 keV are obtained for $Am^{246}$ if one uses an $L$ binding energy of 23·6 keV (the $L_{II}$ absorption value for curium).[5] If one assumes these conversion lines are $K$ lines, the associated gamma energies would be 194, 202, 222, 243, and 255 keV, using $K_{abs} = 128{\cdot}1$ keV for curium.[5] With the data available, we are unable to assign these lines definitely to either $Pu^{246}$ or $Am^{246}$, since all would decay with the same half-life in the equilibrium sample.

A Fermi plot of the data indicated a single high-energy beta group with an endpoint of $1{\cdot}35 \pm 0{\cdot}02$ MeV (Fig. 2). However, low-abundance components would not have been detected because of the low counting rates observed. An indication of a low-energy beta group (probably belonging to $Pu^{246}$) was seen, but no endpoint could be obtained for it, since it was masked by the conversion electron lines.

[4] M. E. ROSE, privately circulated tables.
[5] S. FINE and C. F. HENDEE *Nucleonics* **13**, No. 3, March 1955.

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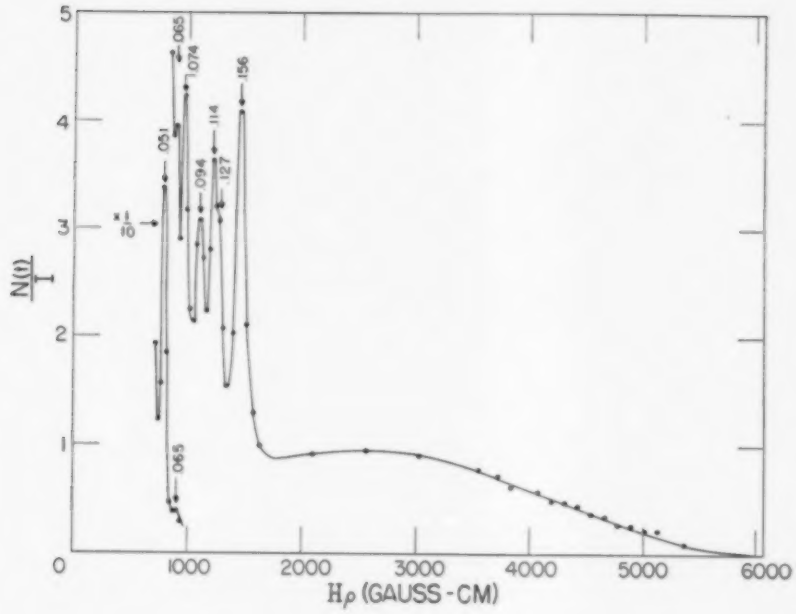


FIG. 1.

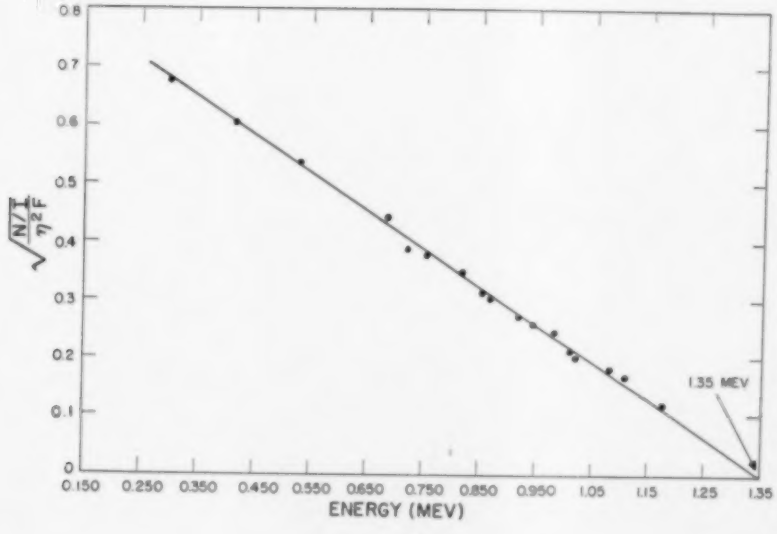


FIG. 2.

The beta radiation from the equilibrium sample was also examined with a Pilot Chemicals, Inc., "Plastifluor B" beta scintillation crystal, 0·8 in. in diameter and 0·8 in. thick, packed in $Al_2O_3$ and covered with l-mil aluminium foil. The crystal was coupled to a Du Mont 6292 photomultiplier tube and used in conjunction with a 10-channel pulse-height analyser. Fermi plots of the beta radiation of $P^{32}$ (1·701 MeV), $Y^{91}$

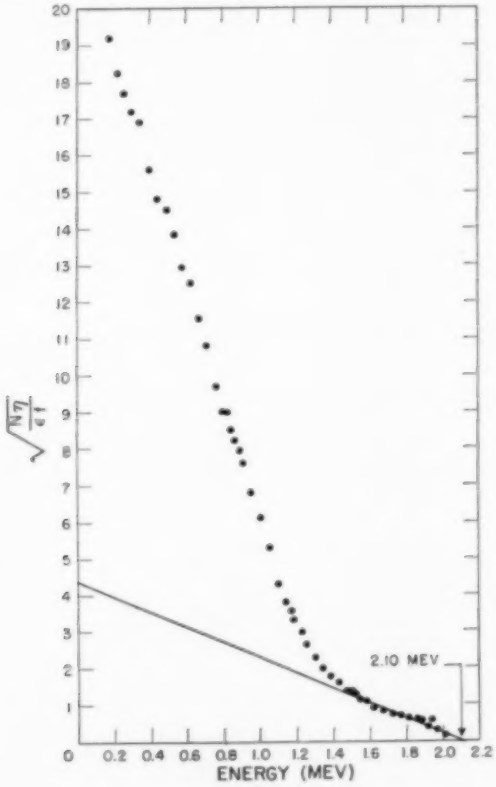


FIG. 3.

(1·537 MeV), and $Tl^{204}$ (0·765 MeV) were used for calibration. A Fermi plot of the data taken on the $Pu^{246}$-$Am^{246}$ equilibrium sample is shown in Fig. 3. It is apparent that there is a rather low abundance (7%) component, with an endpoint energy of about 2·10 MeV. After subtraction of this component, the Fermi plot shown in Fig. 4 was obtained. There also appears to be a component at 1·60 MeV (14%) and a very abundant group (79%) with an endpoint energy of 1·31 MeV, which is in fair agreement with the result obtained from the magnetic spectrometer. The log *ft* values were calculated to be 8·0 for the 2·1 MeV, 7·3 for the 1·60 MeV, and 6·1 for the 1·31 MeV beta groups, respectively.

*Gamma Radiation*

The gamma radiation of $Am^{246}$ alone, and of the equilibrium $Pu^{246}$-$Am^{246}$ sample, was studied with 1-in. diameter by 1½-in.-thick NaI(Tl) crystals in conjunction with multichannel pulse-height analysers (Figs. 5, 6, and 7). The areas of the various

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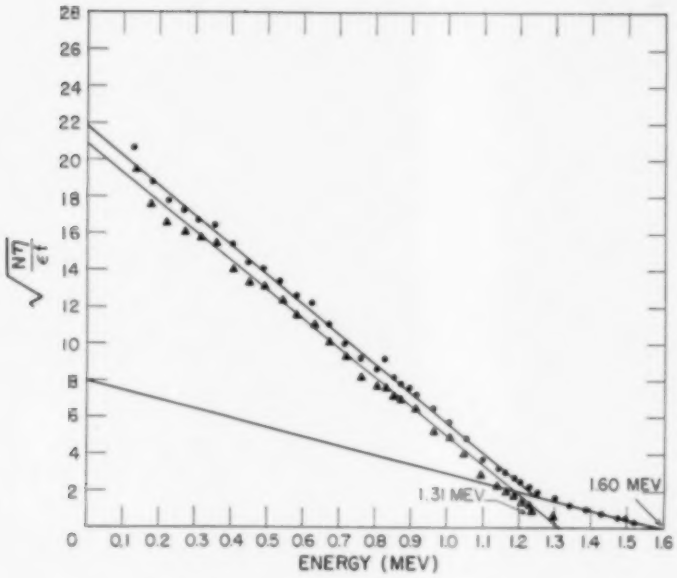


FIG. 4.

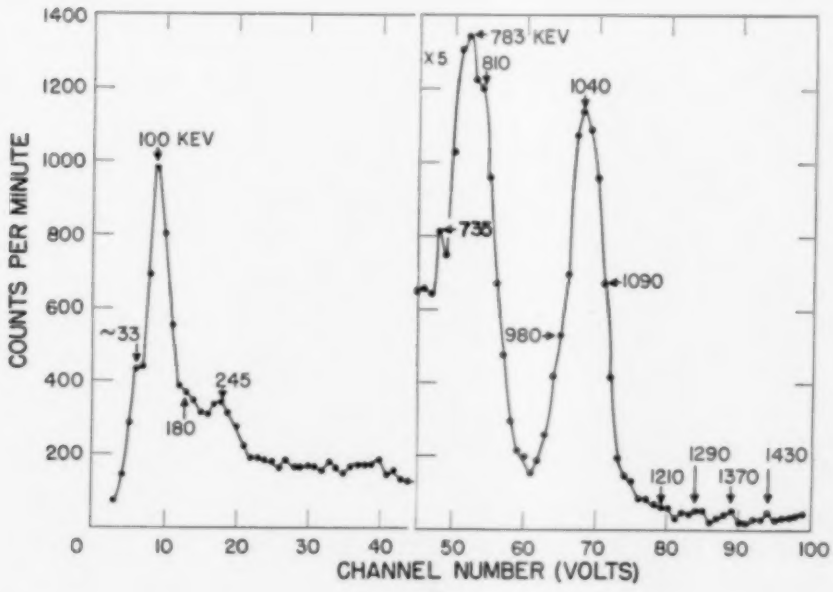


FIG. 5.

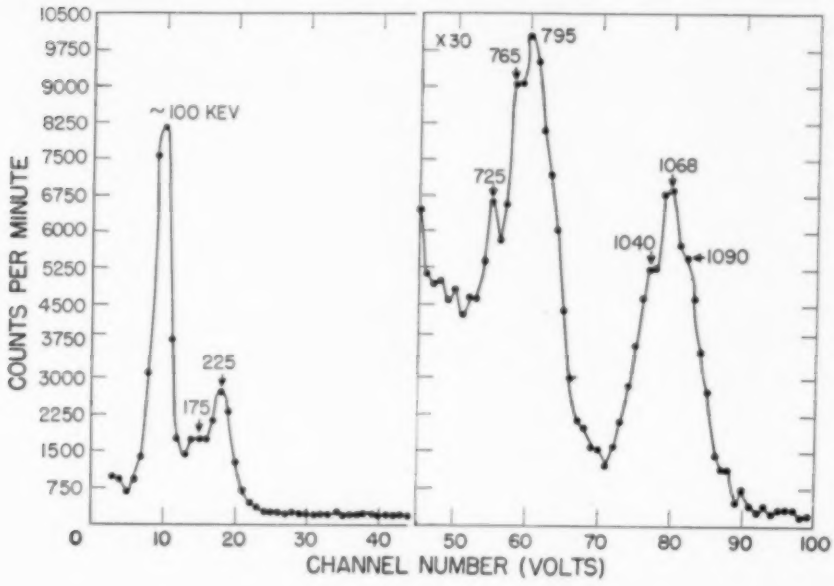
COUNTS PER MINUTE
CHANNEL NUMBER (VOLTS)
~100 KEV
225
175
X30
795
765
725
1068
1040
1090

FIG. 6.

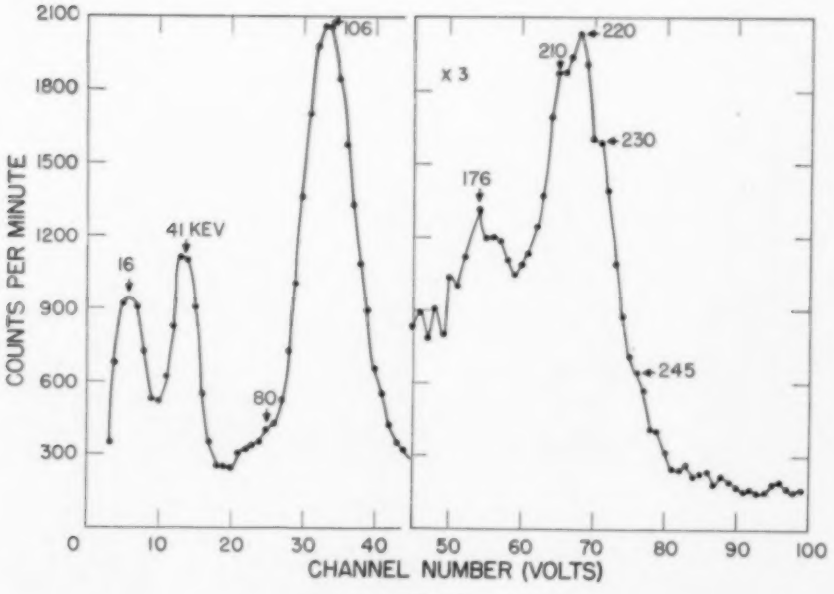
COUNTS PER MINUTE
CHANNEL NUMBER (VOLTS)
106
41 KEV
16
80
X 3
220
210
230
176
245

FIG. 7.

gamma-ray peaks relative to the area of the 1·06 MeV gamma ray were compared, and a similar comparison of the peak heights was made (Table 1). Since the measurements on both samples were performed in the same manner, no absorption corrections

TABLE 1.—RATIO OF GAMMA PEAK HEIGHTS AND AREAS RELATIVE TO THE 1060-KEV GAMMA OF $Am^{246}$

| Gamma energy (keV) | 16 | 41 | 100 | 175–180 | 225 | 245 | 780 |
|---|---|---|---|---|---|---|---|
| $Am^{246}$ | | | | | | | |
| Ratio of areas | not seen at this gain | 0·7 (~33 keV) | 2·5 | 0·4 | — | 1·1 | 1·3 |
| Ratio of peak heights | | 1·9 | 4·3 | 1·4 | — | 1·5 | 1·2 |
| $Pu^{246}$-$Am^{246}$ | | | | | | | |
| Ratio of areas | 2·4 | 2·9 | 10·7 | 2·3 | 3·8 | — | 1·3 |
| Ratio of peak heights | 16·5 | 17·2 | 35·2 | 8·0 | 11·7 | — | 1·5 |

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were made. From these ratios it appears that most of the 225-, 175 to 180-, a large amount of the 100-, and all of the 41-keV gamma rays are associated with the decay of $Pu^{246}$. The disintegration energy of $Pu^{246}$ has been reported to be 0·400 MeV, and no gamma rays above 175 keV were observed in the decay.[6] The $Am^{246}$ has a low-intensity gamma ray at 245 keV, possibly contributes to the 175 to 180- and 100-keV peaks, and has a gamma ray of lower energy than the 41-keV $Pu^{246}$ gamma ray, probably at about 35 keV. The 780- and 1060-keV peaks, in particular, are probably complex and consist of at least two or three gamma rays separated by only 20–50 keV.

## 4. COINCIDENCE STUDIES

*Gamma-gamma Coincidences*

A multichannel pulse-height analyser[1] and a Los Alamos Model 300 coincidence unit were used with 1-in.-diameter by 1-in.-thick, and 1-in.-diameter by 1½-in.-thick NaI(Tl) crystals canned in 330 mg/cm² aluminium. The "trigger" channel was moved in 60-keV steps from 50 keV to 1105 keV, while the other channel was set at its minimum and maximim values so that the gamma radiation in coincidence with the trigger region could be pulse-analysed with the 10-channel analyser. The gain was then increased to cover only the region from 18 to 350 keV and the trigger was varied from 715 to 1165 keV in ~50-keV steps. The gain was increased again by a factor of 2 and a similar series of measurements was made. The results of several runs are summarized in Table 2.

*Gamma-beta Coincidences*

The crystal used for beta-ray spectra measurements was substituted for one of the NaI(Tl) crystals in the coincidence arrangement. By triggering with the 33 to 60-, 95 to 140-, 150 to 202-, 230 to 265-, 730 to 880-, and 1000 to 1150-keV gamma-ray

[6] D. C. HOFFMAN and C. I. BROWNE Radiations of Plutonium-246, *J. Inorg. Nucl. Chem.* **2**, 209 (1956).

TABLE 2.—GAMMA-GAMMA COINCIDENCES ON $Pu^{246}$-$Am^{243}$ EQUILIBRIUM SAMPLE

A. ~80–1500 keV observed in nontrigger channel

| Gamma trigger region (keV) Gain: 150–1500 keV (1½-in. NaI(Tl) crystal) | Gammas in coincidence (1-in. NaI(Tl) crystal) | Relative intensity* (counts/minute) |
|---|---|---|
| 50–115 | <80 | >400 c/m |
| | 135 | 20–30 |
| | 800 | 4·5 |
| | 1060 | 3·6 |
| 115–180 | 105 | 83 |
| | 225 | 6 |
| | 650 | 9 |
| | 820 | 9 |
| | 1060 | 0·6 |
| 180–240 | 120 | 18 |
| | 225 | 9 |
| | 600‡ | 20 |
| | 820‡ | 32 |
| 240–305 | 135 | 9 |
| | 225–250 | 6 |
| | 560–580 | 4 |
| | 825 | 8 |
| | 1090 | 2·5 |
| 305–370 | 135 | 4 |
| | 210 | 4 |
| 370–435 | 200–260‡ | ~4 |
| 435–560 | 225‡ | 16 |
| 560–625 | 225 | 23 |
| 615–675 | 200 | 13·5 |
| 675–735 | 105 | 22 |
| | 230‡ | 10·5 |
| 735–800 | 105 | 26 |
| | 150 | 11 |
| | 220 | 40 |
| 800–860 | 105 | 10 |
| | ~150 | 10 |
| | 220 | 50 |
| | 690 | 1 |
| 860–920 | 105 | 5 |
| | 220–230‡ | 10 |
| 920–980 | 230 | 2 |
| 980–1040 | 270 | 4 |
| 1040–1105 | 270 | 2 |
| 950–1090 | 100 | 16 |
| | 230 | 3·6 |

B. 18–380 keV observed in nontrigger channe

| Gamma trigger region (keV) Gain: 35–1300 keV (1-in. NaI(Tl) crystal) | Gammas in coincidence (1½-in. NaI(Tl) crystal) | Relative intensity* (counts/minute) |
|---|---|---|
| 715–765 | <18 | 5·5 |
| | 75 | 1·0 |
| | 100 | † |
| | 218 | 2·5 |
| 765–820 | <18 | 8·8 |
| | 75 | 1·0 |
| | 108 | 5·0 |
| | 129 (?) | 0·5 |
| | 136 | 0·5 |
| | 227 | 2·3 |
| 820–875 | <18 | 4·5 |
| | 58 | 0·5 |
| | 76 | 1·5 |
| | 108 | 3·8 |
| | 153 (?) | 0·3 |
| | 206 (?) | 1·0 |
| | 223 | 6·5 |
| 875–925 | <18 | 2·0 |
| | 108 | 1·5 |
| | 124 | 1·3 |
| | 173 | 1·3 |
| | 215‡ | 3·6 |
| 910–960 | <18 | 2·0 |
| | 35 (?) | 0·3 |
| | ~100 | † |
| 960–1010 | <18 | 16 |
| | 65 (?) | 0·4 |
| | 85 (?) | 0·4 |
| | 110 | 1·8 |
| | 145 (?) | 1·0 |
| 1010–1065 | <18 | 5·0 |
| | 47 | 0·7 |
| | 75 | 0·7 |
| | 120 | 3·0 |
| | 135–140 | 1·5 |
| | 175 | 0·3 |
| 1065–1115 | <18 | 3·0 |
| | ~30 | 0·9 |
| | 50 | 0·6 |
| | ~70 | 0·3 |
| | 120 | 2·8 |
| | 175 | † |
| 1115–1165 | <18 | 0·8 |
| | ~42 | 0·2 |
| | ~70 | 0·2 |
| | 110‡ | 1·2 |
| | 175 | 0·1 |

TABLE 2 (*cont.*)

C. 9–170 keV observed in nontrigger channel

| Gamma trigger region (keV) Gain: 150–1500 keV (1½-in. NaI(Tl) crystal) | Gammas in coincidence (1-in. NaI(Tl) crystal) | Relative intensity* (counts/minute) |
|---|---|---|
| 670–760 | 18‡ | 10 |
| | 33 | 2 |
| | ~40‡ | 4 |
| | 76 | 2 |
| | 105‡ | 16 |
| 760–820 | 22‡ | 12 |
| | 33 | 4 |
| | 49 | 2 |
| | 100–115‡ | 16 |
| 820–905 | 19 | 8 |
| | 29 | 3 |
| | 36 | 0·5 |
| | 58 | 0·5 |
| | 73 | 2 |
| | ~100‡ | 15 |
| 905–995 | 18 | 2 |
| | 25 | 2 |
| | 34 (?) | 1·4 |
| | ~100‡ | 5·0 |
| 995–1050 | 18 | 2·0 |
| | 25 | 5·0 |
| | ~40 | 0·5 |
| | 50 (?) | 1·0 |
| | ~100‡ | 5·0 |
| 1050–1110 | 20 | 5 |
| | ~36 | 1·6 |
| | 40–80 | † |
| | ~100‡ | 15·0 |

D. 670–1180-keV region observed in non-trigger channel

| Gamma trigger region (keV) Gain: 9–175 keV (1-in. NaI(Tl) crystal) | Gammas in coincidence (1½-in. NaI(Tl) crystal) | Relative intensity* (counts/minute) |
|---|---|---|
| 79–86 | 810 | 4·9 |
| | 1020 | 4·2 |
| 86–93 | 795 | 5·5 |
| | 1020 | 6·6 |
| 93–100 | 795 | 9·1 |
| | 1020 | 13·1 |
| 100–107 | 795 | 12·0 |
| | 1000 | 20·0 |
| 107–113 | 795 | 7·9 |
| | 990 | 10·6 |
| 113–120 | 775 | 4·2 |
| | 990 | 6·9 |

* Counts/minute are reported as actually observed. No absorber or efficiency corrections have been made. Since the intensity of the triggers varies widely, these figures are directly comparable only within a given trigger region.
† Region not checked.
‡ Complex peak.

TABLE 3.—GAMMA-BETA COINCIDENCES ON $Pu^{246}$-$Am^{246}$ EQUILIBRIUM SAMPLE

| Gamma trigger region (keV) | 33–60 | 95–140 | 150–200 | 230–265 | 730–880 | 1000–1150 |
|---|---|---|---|---|---|---|
| Observed Beta Groups (keV) | 2100 ? | | 2100 ? | | | |
| | 1680 ? | 1680 (6%) | 1680 (12%) | | 1520 (55%) | |
| | 1320 ? | 1320 (28%) | 1310 (88%) | 1350 (~100%) | | 1320 (75%) |
| | 1100 (~100%) | 1100 (65%) | 1100 (?) | | 1110 (45%) | 1030 (25%) |

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regions, the beta-ray groups in coincidence with these regions were observed (Table 3). As an example, Fig. 8 shows the Fermi plot of the beta spectrum in coincidence with the 730 to 880-keV gamma region. The decay energy of 2·41 ± 0·10 MeV is established by the coincidences observed between the 1520-keV beta-ray and the 730–880 keV gamma-ray trigger, and between the 1320-keV beta-ray and the 1000–1150-keV gamma-ray trigger.

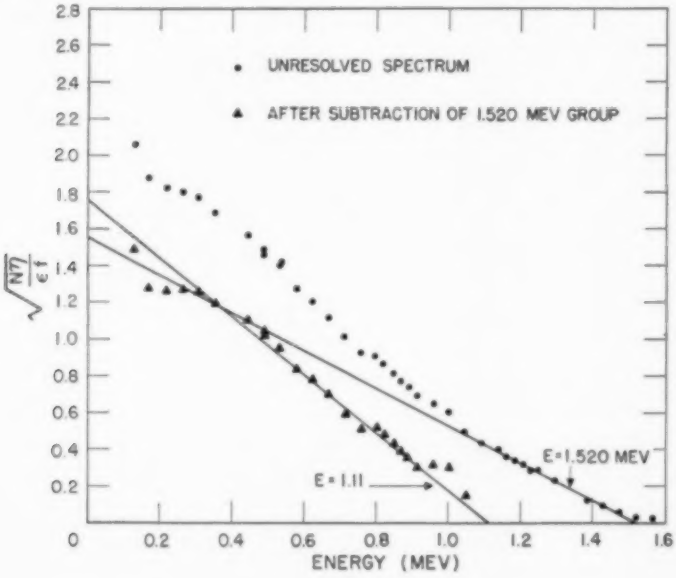
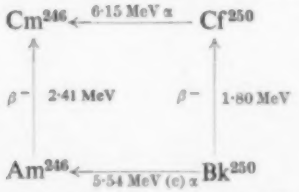



FIG. 8.

The datum that the 800-keV gamma ray is not in coincidence with the 1350-keV beta group introduces a difficulty which is perhaps best resolved by the assumption of complexity in the levels in the vicinity of 890 keV. Such an assumption is consistent with other data, and similar complexities have been observed in other heavy nuclides.

## DISCUSSION

The decay energy of 2·41 MeV obtained from the beta-gamma coincidence studies may be used in the usual manner of closed-cycle calculations in the following cycle:




where the energies used are those of GHIORSO *et al.*,[7] for $Cf^{250}$ alpha decay and $Bk^{250}$ beta decay. The resulting 5·54 MeV for the alpha-decay energy of $Bk^{250}$ does not reflect the effect of a 152-neutron closed subshell, as postulated by GHIORSO *et al.*,[8]

[7] A. GHIORSO, S. G. THOMPSON, G. R. CHOPPIN, and B. G. HARVEY *Phys. Rev.* **94**, 1081 (1954).
[8] A. GHIORSO, S. G. THOMPSON, G. H. HIGGINS, B. G. HARVEY, and G. T. SEABORG *Phys. Rev.* **95**, 293 (1954).

to nearly the extent of the $Cf^{252}$ and $Cf^{250}$ data upon which the subshell prostulate is based. It seems doubtful that our decay energy is in error by more than 100 keV, and even allowing this error to be in the proper direction, it cannot raise the $Bk^{250}$ alpha-decay energy enough to bring this value into agreement with the 5·76 MeV estimated by GLASS[9] on the basis of the californium analogy. To draw any conclusion other than that the subshell effect is certainly not very marked is beyond the limits of accuracy of these data.

The coincidence data indicate that the decay of $Am^{246}$ must be quite complex. However, from the gamma-beta coincidence data, Table 3, one may note that the principle mode of beta decay is probably to a level in the vicinity of 1 MeV. More accurate measurements of the gamma-ray energies need to be obtained, possibly from permanent-magnet spectrographs or by beta spectrometry of radiator sources, before the formulation of a complete decay scheme or a comparison with the levels predicted by the Bohr-Mottelson theory[10] can be made.

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[9] R. A. GLASS, S. G. THOMPSON, and G. T. SEABORG *J. Inorg. Nucl. Chem.* **1**, 1 (1955).
[10] A. BOHR and B. R. MOTTELSON *Kgl. Danske Videnskab, Selsk.* **27**, (1953), No. 16.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 104 to 124. Pergamon Press Ltd., London

# ALKYL AND ARYL DERIVATIVES OF $\pi$-CYCLOPENTADIENYL COMPOUNDS OF CHROMIUM, MOLYBDENUM, TUNGSTEN, AND IRON

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**Abstract**—The preparation of alkyl and aryl $\pi$-cyclopentadienyl carbon monoxide or nitric oxide compounds of Cr, Mo, W, and Fe is described. The methods involve the reaction of halides such as $\pi$-$C_5H_5Cr(NO)_2I$ with Grignard reagents, the reaction of $\pi$-$C_5H_5Mo(CO)_3H$ with diazomethane, and the reaction of sodium salts such as $\pi$-$C_5H_5Fe(CO)_2Na$ with alkyl or aryl halides.

The properties and infra-red spectra of the compounds, and high-resolution nuclear magnetic-resonance spectra of some of these and other cyclopentadienyl compounds are given.

The structure, stabilities, and some reactions of the alkyl, aryl, and $\sigma$-cyclopentadienyl derivatives and of the $\pi$-cyclopentadienyl-tricarbon monoxide hydrides of Cr, Mo, and W are discussed.

The compound $\pi$-$C_5H_5Mo(CO)_2NO$, the halides $\pi$-$C_5H_5Mo(CO)_3X$, and the methyl compound $(\pi$-$C_5H_5)_2Ti(CH_3)_2$ are also described.

## 1. INTRODUCTION

THE number of well characterized organometallic compounds, that is to say compounds with a metal-to carbon $\sigma$-bond, of the transitional metals, is few,[1a] Methyl platinum derivatives are firmly established, and the work of HERMAN and NELSON[1b] conclusively showed the existence of aryl titanium compounds. Naphthyl derivatives of cobalt have been reported, but require further characterization. The existence of numerous "polyphenyl" chromium compounds, originally studied by HEIN, is certain, but it is not proved that there is a metal-to-carbon $\sigma$-bond present in these compounds; indeed, a new type of structure recently proposed for these chromium derivatives by ZEISS and TSUTSUI[1c] involves the direct bonding of a benzene nucleus to the metal atom in a manner analogous to that of the cyclopentadienyl ring in the now well-known $\pi$-cyclopentadienyl metal compounds of which ferrocene is the prototype, and would require the use of two $\pi$-electrons of the ring in metal-ring bonding.†

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† *Note added in proof*—

ZEISS and TSUTSUI's proposal concerning the structures of HEIN's compounds has been given strong support by the recent preparation of di(benzene) chromium, $(C_6H_6)_2Cr$, by E. O. FISCHER and W. HAFNER (*Z. Naturforsch.* **106**, 665, 1955). This compound, which can be regarded as the parent compound from which HEIN's compounds can in principle be derived, may be considered as electronically analogous to ferrocene, with two $\pi$ electrons from each ring being involved in the primary metal to ring bond. Two members of the isoelectronic series $C_4H_4^{2-}$, $C_5H_5^-$, $C_6H_6$, $C_7H_7^+$ have thus now been shown to form "sandwich" type compounds with transitional metals; the possibility that the first member can form metal compounds has been discussed by H. C. LONGUET-HIGGINS and L. E. ORGEL (Chemical Society Discussion, London, December 1955, see *Chemistry and Industry*, 153, 1956), whilst the possiblity that the last member, the tropylium ion, can form sandwich-type compounds where a transition metal can be obtained in a system with a formal negative charge, e.g., as in $C_7H_7Re(CO)_3$, is currently being investigated.

See now: E. O. FISCHER, S. HAFNER, and H. O. STAHL *Z. anorg. Chem.* **282**, 47 (1956).

It would seem that the compound $\pi$-$C_5H_5Cr(NO)_2C_6H_5$ described in this paper is the only chromium phenyl derivative known at the present time.

(1) (*a*) For complete references to the literature: see F. A. COTTON *Chem. Reviews* **55**, 551 (1955). (*b*) D. F. HERMAN and W. K. NELSON *J. Amer. Chem. Soc.* **75**, 3877, 3882 (1953). (*c*) H. H. ZEISS and M. TSUTSUI Abstracts of Papers presented at the 126th meeting of the American Chemical Society, New York, September 1954, p. 29–O; *cf.* also ref. (1a), p. 569.

Recently, the preparations of mononuclear π-cyclopentadienyl carbon monoxide and nitric oxide metal halides,[2, 3] e.g. $\pi$-$C_5H_5Fe(CO)_2Cl$, $\pi$-$C_5H_5Cr(NO)_2Cl$, and of the related hydrides and the salts,[4, 5] e.g. $\pi$-$C_5H_5Cr(CO)_3H$, $\pi$-$C_5H_5Fe(CO)_2Na$, have been described.

From compounds of these types, by the preparative methods outlined below, we have been able to prepare a number of compounds with a transitional metal-to-carbon σ-bond, e.g. $\pi$-$C_5H_5W(CO)_3CH_3$, $\pi$-$C_5H_5Fe(CO)_2C_6H_5$, of considerable stability. In addition to the alkyl and aryl compounds, derivatives in which a cyclopentadienyl group is bound to the metal atom by a σ-bond to a carbon atom have been characterized, e.g. $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$.

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### 1.1. *The Grignard Method*

The preparation of several compounds from the π-cyclopentadienyl carbon monoxide or nitric oxide metal halides by this classical method has been noted in preliminary communications,[6, 7, 8] e.g. $\pi$-$C_5H_5Cr(NO)_2I + CH_3MgI \rightarrow \pi$-$C_5H_5$-$Cr(NO)_2CH_3 + MgI_2$. The method is not uniformly successful, and the yields of the products depend very much on the natures of the reactants; thus, the action of phenyl magnesium bromide on $\pi$-$C_5H_5Mo(CO)_3I$ does not produce the corresponding aryl, but instead gives a high yield of the binuclear compound $\pi$-$C_5H_5Mo(CO)_6$-$Mo\pi$-$C_5H_5$. The yields of the Grignard reactions of π-cyclopentadienyl metal halides are generally somewhat erratic and the values recorded subsequently are only approximate.

The use of sodium cyclopentadienide in tetrahydrofuran as a reagent for the preparation of derivatives with a cyclopentadienyl ring σ-bonded to a metal atom falls, of course, in this class. The first reported use of this procedure, with $\pi$-$C_5H_5Fe(CO)_2Br$, was by HALLAM and PAUSON,[9] but the nature of the product, $\pi$-$C_5H_5Fe(CO)_2\sigma$-$C_5H_5$, was not appreciated by these authors.

The Grignard procedure has also been used to prepare $(\pi$-$C_5H_5)_2Ti(CH_3)_2$ from $(\pi$-$C_5H_5)_2TiCl_2$.

### 1.2. *Reaction of Diazo Compounds with Hydrides*

The discovery of the π-cyclopentadienyl carbon monoxide hydrides of Cr, Mo, and W[4], suggested that alkyl derivatives could be made by a reaction with diazomethane or similar compounds, according to the equation, e.g.

$$\pi\text{-}C_5H_5Mo(CO)_3H + CH_2N_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3CH_3 + N_2$$

The preparation of $\pi$-$C_5H_5Mo(CO)_3CH_3$ by this method was reported in a preliminary note,[7] while in a review article, E. O. FISCHER[5] independently reported the similar preparation of tungsten methyl and ethyl compounds; details of his work

[2] T. S. PIPER, F. A. COTTON, and G. WILKINSON *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[3] T. S. PIPER and G. WILKINSON *ibid.* **2**, 38 (1956).
[4] E. O. FISCHER and W. HAFNER *Z. Naturforsch* **10b**, 140 (1955).
[5] E. O. FISCHER *Angew Chem.* **67**, 475 (1955).
[6] T. S. PIPER and G. WILKINSON *Chem. and Ind.* **41**, 1296 (1955).
[7] T. S. PIPER and G. WILKINSON *Naturwiss.* **42**, 625 (1955).
[8] T. S. PIPER and G. WILKINSON *ibid*, **43**, 15 (1956).
[9] B. F. HALLAM and P. L. PAUSON *Chem. and Ind.* **23**, 653 (1955).

are not yet available.* Since we were unable to obtain high yields with molybdenum, this method of preparation of alkyls was abandoned in favour of Method 3.

1.3. *Reaction of Alkyl and Aryl Halides with Sodium Salts of π-Cyclopentadienyl Compounds*

By the reaction of alkyl or aryl halides with the sodium salt of the π-cyclopentadienyl metal derivative we have been able to prepare numerous alkyl and aryl compounds of Cr, Mo, W, and Fe. The reactions, which are of the type:

$$\pi\text{-}C_5H_5Fe(CO)_2Na + C_2H_5I \rightarrow \pi\text{-}C_5H_5Fe(CO)_2C_2H_5 + NaI$$

in some cases give almost quantitative yields of the desired products. This procedure is potentially applicable for the preparation of compounds with σ-bonds between a transitional element and elements other than carbon by use of suitable halides.*

The alkyl and aryl compounds described in this paper are listed in Table 1 together with the preparative method and the yield, the colours, and the melting-point of the compounds.

Whilst derivatives of chromium, molybdenum, tungsten, and iron have, so far, been prepared, there now seems to be no reason why similar derivatives of other transitional metals cannot be made. In fact, since all the alkyls and aryl compounds obey the structural principles for mononuclear π-cyclopentadienyl compounds discussed previously,[2] one can indeed expect that, provided the starting materials suitable for use in the preparative procedures outlined above become available, as yet unmade compounds, e.g. $\pi\text{-}C_5H_5Mn(NO)(CO)CH_3$, should be reasonably stable.

Some other π-cyclopentadienyl compounds prepared during the course of these studies, e.g. $\pi\text{-}C_5H_5Mo(CO)_2NO$, $\pi\text{-}C_5H_5Mo(CO)_3Cl$, and some of the reactions of $\pi\text{-}C_5H_5Mo(CO)_3H$, are described in the experimental section.

## 2. EXPERIMENTAL

### *Preparations*

All the preparations described below were carried out in a nitrogen atmosphere. Tetrahydrofuran was purified before use by distillation in nitrogen over lithium aluminium hydride. We are deeply indebted to Dr. E. O. BRIMM and the Linde Air Products Company, Tonawanda, N.Y., for several gifts of chromium, molybdenum, and tungsten hexacarbonyls, and to the Climax Molybdenum Company, New York, N.Y., for the welcome gift of several pounds of molybdenum hexacarbonyl.

2.1. *Alkyl and Aryl Compounds by the Grignard Procedure (Method I)*

The halides $\pi\text{-}C_5H_5Cr(NO)_2Br$ and $\pi\text{-}C_5H_5Fe(CO)_2I$ in dilute ether solution (0·02 to 0·1 molar) were treated with the appropriate Grignard reagent in ether or with sodium cyclopentadienide in tetrahydrofuran. Stoichiometric quantities of the reactants were used in all cases, and the Grignard or sodium cyclopentadienide solution was added to the halide solution dropwise with brisk stirring. The mixtures were then stirred rapidly for two to three hours at 25° and the solvent was then removed.

From the residue, methyl compounds, $\pi\text{-}C_5H_5Cr(NO)_2CH_3$ and $\pi\text{-}C_5H_5Fe(CO)_2CH_3$, were isolated by vacuum sublimation to an ice-cooled probe; the ethyl compounds were also isolated directly by sublimation, and it was necessary to cool the probe with dry ice.

The phenyl and σ-cyclopentadienyl derivatives were isolated by chromatography; the compounds were extracted from the reaction residue with petroleum ether (30–60°) and were transferred in this

* *Note added in proof*—
The compound $\pi\text{-}C_5H_5Fe(CO)_2Si(CH_3)_3$ has now been prepared by the reaction of $\pi\text{-}C_5H_5Fe(CO)_2Na$ with trimethylchlorosilane (T. S. PIPER, D. LEMAL, and G. WILKINSON *Naturwiss.* **43**, 129, 1956).
See now: E. O. FISCHER, S. HAFNER, and H. O. STAHL *Z. anorg. Chem.* **282**, 47 (1956).

TABLE 1.—ALKYL AND ARYL DERIVATIVES OF π-CYCLOPENTADIENYL METAL COMPOUNDS

| Compound | Preparation* | Purification† | Yield % | Colour | m.p. °C |
|---|---|---|---|---|---|
| $\pi$-$C_5H_5Cr(NO)_2CH_3$ | I | A | 60 | dark green | 82·8–83·2 |
| $\pi$-$C_5H_5Cr(NO)_2CH_2Cl$§ | II (on chloride) | B | 3 | green | 71 |
| $\pi$-$C_5H_5Cr(NO)_2C_2H_5$ | I | A | 5 | green | oil |
| $\pi$-$C_5H_5Cr(NO)_2C_6H_5$ | I | BA | 0·5 | green | oil |
| $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$ | Ia | BA | 20 | brown | 66.5–67·2 |
| $\pi$-$C_5H_5Cr(CO)_3CH_3$‡ | III | A | 1–3 | yellow | — |
| $\pi$-$C_5H_5Mo(CO)_3CH_3$ | II | A | 4 | yellow | 124 (d) |
| | III | A | 85 | | |
| $\pi$-$C_5H_5Mo(CO)_3C_2H_5$ | III | A | 78 | yellow | 77·5–78·5 (d) |
| $\pi$-$C_5H_5Mo(CO)_3isoC_3H_7$ | III | A | 5 | yellow | 29–30 |
| $\pi$-$C_5H_5W(CO)_3CH_3$ | III | A | 80 | lemon yellow | 144·7–145·3 |
| $\pi$-$C_5H_5W(CO)_3C_6H_5$ | III | A | 75 | yellow | 93·0–93·5 (slight d) |
| $\pi$-$C_5H_5Fe(CO)_2CH_3$ | I | A | 50 | caramel | 78–82 |
| | III | A | 70 | (waxy) | |
| $\pi$-$C_5H_5(CO)_2C_2H_5$ | III | A | 60 | caramel | oil |
| $\pi$-$C_5H_5Fe(CO)_2\sigma$-$C_5H_5$ | Ia | BA | 15 | orange | 46 |
| $\pi$-$C_5H_5Fe(CO)_2C_6H_5$ | I | BA | 5 | caramel | 26–30 |
| | III | BA | 2 | | |
| $(\pi$-$C_5H_5)_2Ti(CH_3)_2$ | I | A | 1 | orange-yellow (waxy) | decomp. ~100 |

*I = Grignard reagent in ether on the bromide or iodide compounds.
Ia = Sodium cyclopentadienide in tetrahydrofuran on the bromide or iodide compounds.
II = Diazomethane reaction.
III = Alkyl or aryl iodide on the sodium salt $\pi$-$C_5H_5M(CO)_3Na$.
† Isolation from the evaporated reaction mixture: *A* by direct sublimation in vacuum; *B* by extraction with petroleum ether (30–60°) and chromatographic separation on alumina using benzene-petroleum ether mixtures.
‡ Compound identified by infra-red spectrum only.

solvent to an alumina column. The products were eluted with petroleum ether-benzene mixtures. The preparation of $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$ from 2·6 g (0·1 mole) of $C_5H_5Cr(NO)_2Br$ may be taken as an example. The residue from the reaction with sodium cyclopentadienide after removal of solvent was extracted with 200 ml petroleum ether and the filtered extract passed through 30 g alumina in a small column. Using 50-ml portions, the column was washed with petroleum ether containing first 10%, then 20% of benzene. Subsequently the desired product was eluted from the column with a 2 : 1 mixture of petroleum ether and benzene. The progress of the separation was checked by measurement of the infra-red spectrum of the various fractions obtained.

After chromatographic separation, the products were sublimed at ~50°C at $10^{-3}$ mm Hg, and collected on an ice-cooled probe. The π-cyclopentadienyl metal bromide compounds can be used in these preparations, and give yields comparable to those using the iodides. For the chlorides, however, the yield of the alkyl and aryl compounds is often greatly reduced and in some cases no product can be isolated. A summary of the preparations of the alkyl and aryl derivatives by the Grignard method is presented in Table 2. The reaction conditions are as stated above, except where noted. Standardized Grignard reagents were used throughout. Column 4, labelled addition, gives the yield of the alkyl or aryl derivative. Column 5, labelled reduction, gives the yield of the appropriate binuclear carbon-monoxide compound. In the case of the chromium derivatives, no evidence for the existence of a binuclear nitric-oxide derivative was obtained. Studies of reaction products other than the ones noted here have not been made at the present time.

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TABLE 2.—YIELDS AND PRODUCTS IN GRIGNARD REACTIONS

| Metal derivative | Grignard Reagent | Solvent | Addition | Reduction | Biphenyl | Number of Experiments |
|---|---|---|---|---|---|---|
| $\pi$-$C_5H_5Cr(NO)_2Cl$ | $CH_3MgI$ | $(C_2H_5)_2O$ | 40% | — | — | 2 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $CH_3MgI$ | $(C_2H_5)_2O$ | 60 | — | — | 3 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $CH_3MgI$ | $C_4H_8O$ | trace | — | — | 2 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $CH_3MgI$* | $C_4H_8O$ | 1 | — | — | 1 |
| $\pi$-$C_5H_5Cr(NO)_2I$ | $CH_3MgI$ | $(C_2H_5)_2O$ | 55 | — | — | 1 |
| $\pi$-$C_5H_5Cr(NO)_2Cl$ | $C_2H_5MgBr$ | $(C_2H_5)_2O$ | 0·2 | — | — | 1 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $C_2H_5MgBr$ | $(C_2H_5)_2O$ | 5 | — | — | 2 |
| $\pi$-$C_5H_5Cr(NO)_2Cl$ | $C_2H_5MgBr$ | $(C_2H_5)_2O$ | 0·1 | — | — | 1 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $C_2H_5MgBr$ | $(C_2H_5)_2O$ | 0·5 | — | 53% | 2 |
| $\pi$-$C_5H_5Cr(NO)_2Br$ | $C_2H_5Na$ | $(C_2H_5)_2O$ | 20 | — | — | 2 |
| $\pi$-$C_5H_5Fe(CO)_2Cl$ | $CH_3MgI$ | $C_4H_8O$ | 0 | — | — | 1 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $CH_3MgI$† | $(C_2H_5)_2O$ | 50 | 0 | — | 3 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $CH_3MgI$‡ | $(C_2H_5)_2O$ | 46 | 0 | — | 1 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $C_2H_5MgBr$ | $(C_2H_5)_2O$ | 0 | 17% | — | 1 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $C_6H_5MgBr$§ | $(C_2H_5)_2O$ | 4·7 | 60 | 68 | 1 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $C_6H_5MgBr$ | $(C_2H_5)_2O$ | 3 | 60 | 70 | 2 |
| $\pi$-$C_5H_5Mo(CO)_3I$ | $CH_3MgI$ | $(C_2H_5)_2O$ | 0 | — | — | 2 |
| $\pi$-$C_5H_5Mo(CO)_3I$ | $CH_3MgI$§ | $(C_2H_5)_2O$ | 0 | — | — | 1 |
| $\pi$-$C_5H_5Mo(CO)_3I$ | $C_6H_5MgI$ | $(C_2H_5)_2O$ | 0 | 59 | 72 | 2 |
| $\pi$-$C_5H_5Fe(CO)_2I$ | $C_5H_5Na$ | $(C_2H_5)_2O$ | 15 | 15 | — | 2 |
| $\pi$-$C_5H_5Mo(CO)_3I$ | $C_5H_5Na$ | $(C_2H_5)_2O$ | 0 | — | — | 1 |

* Allowed to stand 15 hours, using a 50% excess of $CH_3MgI$.
† 27% of the starting material $\pi$-$C_5H_5Fe(CO)_2I$ was recovered.
‡ 7 mole % anhydrous cobaltous chloride was added to the reaction mixture.
§ 5 mole % magnesium iodide added.

### 2.2. *Di($\pi$-cyclopentadienyl)-dimethyl-titanium*, $(\pi\text{-}C_5H_5)_2(CH_3)_2Ti$

Various aryl compounds, e.g. $(C_6H_5)_2Ti(\pi\text{-}C_5H_5)_2$, have been prepared[10] by the reaction of lithium aryls with di($\pi$-cyclopentadienyl) titanium halides. In view of the stability of the methyl compounds described in this paper, we attempted the preparation of a methyl titanium derivative by the Grignard method.

To di($\pi$-cyclopentadienyl) titanium dichloride[11] (2 g) in tetrahydrofuran (150 ml) the stoichiometric quantity methyl magnesium iodide was added slowly with stirring at 25°C. The solution darkened initially, but then became orange-yellow. After stirring for two hours, a few millilitres of methanol were added, the solvent was rapidly removed in vacuum, and the residue extracted with petroleum ether. The product was obtained by cooling the filtered petroleum solution to −80°C; it was then purified by sublimation at 40°C at $10^{-4}$ mm Hg. The yield was 30 mg, about 1%; other products of the reaction have not been studied. The compound is an orange-yellow waxy solid, decomposing spontaneously above 100°C. During the sublimation in several preparations, the residue and the sublimate spontaneously decomposed to a black solid. This decomposition is apparently autocatalytic. Careful and rapid separation is therefore necessary.

### 2.3. *$\pi$-Cyclopentadienyl-tricarbon monoxide-methyl-molybdenum*, $\pi$-$C_5H_5Mo(CO)_3CH_3$ *by the Diazomethane Procedure (Method II)*

7·0 g of the hydride, $\pi$-$C_5H_5Mo(CO)_3H$, in 200 ml ether, were treated with about a twofold excess of diazomethane in ether at 0°C for 24 hours. The diazomethane was prepared from N-methyl-N-nitrosourea by the usual procedure. The solvent was removed and the crude product sublimed from

[10] L. SUMMERS, R. H. ULOTH, and A. HOLMES *J. Amer. Chem. Soc.* **77**, 3604 (1955).
[11] G. WILKINSON and J. M. BIRMINGHAM *J. Amer. Chem. Soc.* **76**, 4281 (1954).

the residue in vacuum. It was separated from a red oily material (unidentified) which also sublimed by chromatography on alumina, using benzene-petroleum mixtures. The yield of $\pi$-$C_5H_5Mo(CO)_3CH_3$ was only 0·22 g (3% based on the hydride), and this preparative method was abandoned in favour of the Method III.

### 2.4. *π-Cyclopentadienyl-dinitric oxide-chloromethyl-chromium*

To 0·21 g $\pi$-$C_5H_5Cr(NO)_2Cl$ in 200 ml ether containing 3 millimoles diazomethane at 25°C was added 5–10 g copper powder. The mixture was stirred vigorously for 15 hours. The solvent was removed and the product was extracted with petroleum ether; it was then purified by chromatography on alumina. Yield ~5 mg (~3%, based on the chloride). Due to small and erratic yields and the difficulties in purification on account of the moderately rapid decomposition of the compound by air, characterization of this compound was based on its infra-red spectrum, taken in $CS_2$ and $CCl_4$ solution, which shows two C-H stretching frequencies of the methylene group and a C-Cl stretching frequency at 670 $cm^{-1}$ (vs) in addition to bands characteristic for the ring.

### 2.5. *Alkyl and Aryl Compounds from the Reaction of Alkyl Halides with Sodium Salts (Method III)*

To the tetrahydrofuran solution of $\pi$-$C_5H_5Cr(CO)_3Na$, $\pi$-$C_5H_5Mo(CO)_3Na$, $\pi$-$C_5H_5W(CO)_3Na$, or $\pi$-$C_5H_5Fe(CO)_2Na$ (Preps. 6 and 7), was added the alkyl or aryl iodide in an excess sufficient to react with the total amount of sodium used in the preparations. A rapid reaction occurred with the alkyl iodides, but the mixtures were stirred for a few hours at ~40°C to ensure complete reaction. The reaction of iodobenzene with $\pi$-$C_5H_5Fe(CO)_2Na$ is much slower than with the alkyl iodides, and is incomplete; here, the mixtures were stirred at 25°C for about 4 days. There appears to be no reaction of iodobenzene with $\pi$-$C_5H_5Mo(CO)_3Na$ or with $\pi$-$C_5H_5W(CO)_3Na$.

After the reaction period, the solvent was removed. The alkyl compounds were recovered by direct sublimation in vacuum at ~50°C from the reaction flask to a cooling probe inserted into a neck of the flask. The phenyl iron compound was extracted from the reaction mixture with petroleum ether and was adsorbed from this solution on an alumina column; biphenyl was eluted with petroleum ether + 10% benzene, and the product subsequently eluted with petroleum ether + 30–40% benzene.

In all cases the products were purified by sublimation in vacuum at 25–50°C.

### 2.6. *The Sodium Salts,* $\pi$-$C_5H_5M(CO)_3Na$ *of* Cr, Mo, *and* W

To a solution of sodium cyclopentadienide (0·12 mole) in tetrahydrofuran (200 ml) was added the solid hexacarbonyl (0·1 mole). The solution was refluxed for 12 hours and the solvent removed in vacuum. A test was made for unreacted carbonyl at this point; the stirrer was replaced by a water-cooled probe fitted by a ground joint into the neck of the flask, and the evacuated flask was warmed to ~60°C. Using $Mo(CO)_6$ and $W(CO)_6$, the reaction is essentially complete in 12 hours and little or no carbonyl is recovered; with $Cr(CO)_6$, one-third of the carbonyl is recovered. No attempt has been made to isolate the pure sodium salts, and the products were utilized *in situ* for further reactions.

### 2.7. *The Sodium Salt* $\pi$-$C_5H_5Fe(CO)_2Na$

To 0·5 mole of sodium as 6% sodium amalgam in tetrahydrofuran (100 ml) was added a solution of $(\pi\text{-}C_5H_5)Fe(CO)_4Fe(\pi\text{-}C_5H_5)$[2] (0·1 mole) in tetrahydrofuran (100 ml). The mixture was stirred rapidly for 12 hours, and the product, containing an excess of the amalgam, was used directly in subsequent reactions.

### 2.8. *The π-cyclopentadienyl-tricarbon monoxide-hydrides of* Cr, Mo, *and* W

Only a statement of the method of preparation of these compounds has been previously provided.[4]*

To the dry sodium salts prepared as above (Prep. 6) the theoretical amount (0·12 mole) of glacial acetic acid in tetrahydrofuran (150 ml) was added. The mixture was stirred briefly and the solvent removed in vacuum. The product was then sublimed to a probe cooled to 0°C in vacuum. The

* *Note added in proof*—
See now: E. O. Fischer, W. Hafner, and H. O. Stahl *Z. anorg. Chem.* **282**, 47 (1956).



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chromium hydride sublimes at $10^{-2}$ mm Hg at room temperature, while the tungsten and molybdenum compounds require warming to 50°C.

The yields of $\pi$-$C_5H_5Mo(CO)_3H$ and $\pi$-$C_5H_5W(CO)_3H$ were about 90% for the overall preparation from the hexacarbonyls.

### 2.9. *$\pi$-Cyclopentadienyl-dinitric oxide-chromium Halides*

The following preparation of $\pi$-$C_5H_5Cr(NO)_2Cl$ (or Br) is superior to that given previously.[3] By the reaction of sodium cyclopentadienide with anhydrous chromic chloride, 50 g of $(\pi$-$C_5H_5)_2Cr$[12] was prepared. The crude product was dissolved in ether (700 ml) and a stream of hydrogen halide passed through the solution, with stirring, until the solution, which contains a blue-green suspension of the binuclear $\pi$-cyclopentadienyl chromium bridging halide,[13] was green in colour. A large excess of nitric oxide was then bubbled through the mixture, which was stirred vigorously at 25°C. The solvent was then removed and the product crystallized from dichloromethane. For the *bromide*, 52 g of $\pi$-$C_5H_5Cr(NO)_2Br$ was isolated (yield 65%, based on $CrCl_3$); the compound forms very dark-brown crystals, m.p. 140·5–141°C. The *iodide* was prepared by treating the bromide with the theoretical quantity of aqueous silver nitrate. An excess of concentrated hydriodic acid was added and the iodide was extracted from the aqueous suspension by chloroform. Crystallization from dichloromethane gave a high yield of $\pi$-$C_5H_5Cr(NO)_2I$, m.p. 149–151°C.

### 2.10. *$\pi$-Cyclopentadienyl-tricarbon monoxide-molybdenum Halides,*

$\pi$-$C_5H_5Mo(CO)_3Cl$

The hydride was dissolved in an excess of carbon tetrachloride. The reaction

$$\pi\text{-}C_5H_5Mo(CO)_3H + CCl_4 = \pi\text{-}C_5H_5Mo(CO)_3Cl + CHCl_3$$

was complete in ~20 min at 25°C. The chloride was precipitated quantitatively. It was isolated by filtering the carbon tetrachloride solution as orange-red crystals which decompose at 145°C without melting. (*Analysis*—Required: C 34·25, H 1·8, Cl 12·64, Mo 34·2; found: C 34·8, H 2·0, Cl 12·77, Mo 34·1.) The formation of chloroform in the above reaction was shown by infra-red analysis. The compound $\pi$-$C_5H_5Mo(CO)_3Cl$ is insoluble in water and is decomposed by silver-nitrate solution. Unlike the case of the iron halides, e.g. $\pi$-$C_5H_5Fe(CO)_2Cl$,[2] there is thus no evidence for the formation of cationic species in aqueous solution. The compound is only slightly soluble in petroleum, but is soluble in polar organic solvents without decomposition.

$\pi$-$C_5H_5Mo(CO)_3Br$. This compound was prepared by the reaction of $\pi$-$C_5H_5Mo(CO)_3H$ with *N*-bromosuccinimide in ether solution. The product was crystallized from dichloromethane as red crystals, m.p., 150–151°C. There is no reaction between $\pi$-$C_5H_5Mo(CO)_3H$ and ethyl bromide even on refluxing the mixture for several days.

$\pi$-$C_5H_5Mo(CO)_3I$. The hydride was refluxed with an excess of methyl iodide in benzene for 24 hours. Crystallization of the solid residue from dichloromethane-petroleum ether mixtures by cooling gave a quantitative yield of $\pi$-$C_5H_5Mo(CO)_3I$ as red crystals, m.p. 134–134·5°C. (*Analysis*—Required: C 25·8, H 1·35, I 34·1, Mo 25·8; found: C 25·74, H 1·5, I 34·5, Mo 25·7. Molecular weight by the isopiestic method in dichloromethane: found 375, required 372.) This iodide can also be obtained in ~60% yield by refluxing the mercury salt $[\pi$-$C_5H_5Mo(CO)_3]_2Hg$[4] with iodine in benzene for a few hours.

### 2.11. *$\pi$-Cyclopentadienyl-dicarbon monoxide-iodo-iron.*

This compound was originally prepared[12] by treating $\pi$-$C_5H_5Fe(CO)_4Fe\pi$-$C_5H_5$ with iodine. We have attempted to prepare it by the simpler route

$$Fe(CO)_4I_2 + C_5H_5Na \rightarrow \pi\text{-}C_5H_5Fe(CO)_2I + NaI + 2CO.$$

The iron carbonyl iodide was prepared by the addition of iodine to a slight excess of $Fe(CO)_5$ in ether, and the mixture stirred for 2 hours. One equivalent of sodium cyclopentadienide in tetrahydrofuran was then added, and the mixture stirred for 2 hours. The solvent was removed, and the residue

[12] G. WILKINSON, F. A. COTTON, and J. M. BIRMINGHAM *J. Inorg. Nucl. Chem.* **2**, 95 (1956).
[13] A. K. FISCHER and G. WILKINSON unpublished work.

extracted with 30% benzene in petroleum ether. The product was adsorbed from this solution on an alumina column, and was eluted by a 1 : 1 benzene-petroleum ether mixture. Yield ~10%.

### 2.12. *π-Cyclopentadienyl-dicarbon monoxide-nitric oxide-molybdenum*

2·5 g of $\pi$-$C_5H_5Mo(CO)_2H$ in 100 ml ether was treated with an excess of *N*-methyl-*N* nitroso-*p*-toluene sulphonamide in ether. The solvent was removed and the product sublimed in vacuum at 50°C to an ice-cooled probe. Yield 1·4 g (55%). The compound forms stable orange crystals, m.p. 85·2–85·7°C. It is readily soluble in organic solvents without decomposition. (*Analysis*—Required for $\pi$-$C_5H_5Mo(CO)_2NO$: C 34·0, H 2·0, N 5·67, Mo 38·85; found: C 34·2, H 2·2, N 5·67, Mo 38·66.)

The compound can also be made by the direct action of nitric oxide on $\pi$-$C_5H_5Mo(CO)_2H$, in an organic solvent.

## *B. Properties*

### 2.14. *General Properties of the Alkyl and Aryl Compounds*

Analytical data are presented in Table 3. Whilst only $\pi$-$C_5H_5Cr(NO)_2CH_3$ has been shown to be diamagnetic by direct measurement by the Gouy method, the fact that high-resolution nuclear magnetic-resonance spectra of the compounds can be obtained (*vide infra*) shows that all these compounds are diamagnetic.

All the compounds are readily soluble in petroleum ether (30–60°) and indeed in all common organic solvents; they sublime easily in high vacuum at temperatures from 25–50°C and they have a noticeable camphoraceous odour. In organic solvents, all the compounds are slowly decomposed by air, some more rapidly than others, but the solutions can be preserved in vacuum or in an inert atmosphere.

TABLE 3.—ANALYTICAL DATA*

| Compound | Required | | | | Found | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Metal | C | H | N | Metal |
| $\pi$-$C_5H_5Cr(NO)_2CH_3$† | 37·5 | 4·2 | 14·6 | 27·1 | 37·4 | 4·3 | 14·5 | 27·0 |
| $\pi$-$C_5H_5Cr(NO)_2C_6H_5$ | 49·6 | 4·2 | 11·6 | 21·5 | 49·7 | 4·4 | 11·7 | 21·3 |
| $\pi$-$C_5H_5Mo(CO)_2CH_3$ | 41·6 | 3·4 | | 36·9 | 41·1 | 3·2 | | 37·1 |
| $\pi$-$C_5H_5Mo(CO)_2C_6H_5$ | 43·8 | 3·7 | | 35·0 | 43·8 | 3·76 | | 35·4 |
| $\pi$-$C_5H_5Mo(CO)_2$*iso*-$C_3H_7$ | 45·8 | 4·2 | | | 45·8 | 4·3 | | |
| $\pi$-$C_5H_5W(CO)_2CH_3$ | 31·1 | 2·3 | | 52·85 | 31·1 | 2·5 | | 52·85 |
| $\pi$-$C_5H_5W(CO)_2C_6H_5$ | 33·2 | 2·8 | | 50·5 | 33·3 | 2·8 | | 50·8 |
| $\pi$-$C_5H_5Fe(CO)_2CH_3$ | 50·0 | 4·2 | | 29·1 | 49·0 | 4·2 | | 29·2 |
| $\pi$-$C_5H_5Fe(CO)_2C_2H_5$ | | | | 27·1 | | | | 26·8 |
| $\pi$-$C_5H_5Fe(CO)_2C_6H_5$ | 61·4 | 4·0 | | 22·0 | 62·4 | 4·2 | | 21·8 |
| $(\pi$-$C_5H_5)_2Ti(CH_3)_2$ | 69·3 | 7·8 | | | 68·2 | 7·8 | | |

* Microanalyses by S. NAGY, Massachusetts Institute of Technology and Schwartzkopf Laboratories, Woodside, New York.

† Molecular weight by isopiestic method in dichloromethane; found 188, required 192.

The iron compounds have the lowest stability, both thermally and towards air. The compound $\pi$-$C_5H_5Fe(CO)_2CH_3$, as the solid shows decomposition in air within a few hours; the ethyl compound begins to decompose within 15 min, whilst the phenyl is somewhat more resistant to air than is the methyl compound.

The chromium-nitric oxide derivatives show the same order of stabilities as the iron carbon monoxide derivatives, viz. phenyl > methyl > ethyl, but are more stable; the methyl compound, for example, begins to decompose in air only after a day or two.

The compounds $\pi$-$C_5H_5M(CO)_3R$ of the Group VI elements show great differences in stability,

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both thermally and towards air. The chromium compound, $\pi$-$C_5H_5Cr(CO)_3CH_3$, is rather unstable and is quite readily oxidized by air, and is indeed very difficult, if not impossible, to obtain in a pure state. The molybdenum methyl compound begins to decompose in air after a few days and upon heating in vacuum at 110°C. The tungsten analogue, however, appears to be stable indefinitely in air and melts at 145°C without decomposition; its solutions in organic solvents are quite stable for at least several days.

The ethyl compounds are generally noticeably less stable than the methyl compounds, and the molybdenum isopropyl compound is less stable than the ethyl.

Thermal decomposition of $\pi$-$C_5H_5Mo(CO)_3CH_3$ and $\pi$-$C_5H_5Fe(CO)_2CH_3$ at 110°C has been found to produce the binuclear carbon-monoxide compounds in addition to tarry material.

All the compounds are insoluble in and are unaffected by water, with the exception of $\pi$-$C_5H_5Cr(NO)_2CH_3$, which is slightly soluble in water, giving a faint-yellow solution. Acids and bases attack both the alkyls and aryls. With acids, both the $\pi$-$C_5H_5Fe(CO)_2R$ and $\pi$-$C_5H_5Cr(NO)_2R$ groups of compounds give the cations $[\pi\text{-}C_5H_5Fe(CO)_2]^+$ and $[\pi\text{-}C_5H_5Cr(NO)_2]^+$; these cations (which may well have one firmly co-ordinated water molecule) give precipitates with silicotungstic acid and REINECKE's salt, similar to those given by ions such as $[(\pi\text{-}C_5H_5)_2Fe]^+$. The molybdenum and tungsten compounds slowly decompose with acids and bases, and there is no evidence for the formation of cations. All the alkyl and aryl compounds are attacked by halogens; with iodine, for example, the iodide and the alkyl or aryl halide is formed quantitatively—thus

$$\pi\text{-}C_5H_5Mo(CO)_3CH_3 + I_2 \rightarrow \pi\text{-}C_5H_5Mo(CO)_3I + CH_3I$$

None of these compounds react with ferrous chloride in tetrahydrofuran. With the exception of $\pi$-$C_5H_5Fe(CO)_2\sigma$-$C_5H_5$ and $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$, none react with maleic anhydride in benzene solution; for these two compounds, the addition of maleic anhydride causes a rapid change in colour and the compounds cannot be subsequently recovered; the maleic anhydride adducts were not sufficiently stable to allow isolation and characterization.

## 2.15. *Some Properties of the $\pi$-Cyclopentadienyl-tricarbon monoxide Hydrides of* Cr, Mo, *and* W

These three compounds form yellow crystals; the increase in stability with increasing atomic number is noteworthy. The chromium compound,[4] $\pi$-$C_5H_5Cr(CO)_3H$ is instantaneously oxidized by air both as the solid or in solution and also decomposes at its melting-point 57–58°C. Solutions of $\pi$-$C_5H_5Mo(CO)_3H$ are also instantaneously decomposed by air, but the crystals require several minutes for complete decomposition; the compound melts at 54–55°C, and thermal decomposition in vacuum begins at about 110°C. The stability of $\pi$-$C_5H_5W(CO)_3H$ (m.p. 68·5–69·5°C) is considerable; complete oxidation of the solid in air requires several days, and decomposition of the solutions by air is noticeable only after 15 min or so. The solid is stable in vacuum up to 180°C. In all three cases, thermal decomposition gives the binuclear compounds $\pi$-$C_5H_5M(CO)_6M\pi$-$C_5H_5$.

It is interesting to note that in nonpolar solvents such as petroleum ether, the compounds $\pi$-$C_5H_5M(CO)_3H$ are decomposed to a black mass by air. In polar solvents, however, particularly in tetrahydrofuran, smooth oxidation to $\pi$-$C_5H_5M(CO)_6M\pi$-$C_5H_5$ occurs; studies on the mechanism of these oxidations are in progress. In this way, we prepared the molybdenum compound[7] in 70% yield; this compound has properties essentially identical with those reported for the compound $C_5H_5Mo(CO)_5MoC_5H_5$.[14] As noted earlier,[7] it must be presumed that the only binuclear molybdenum compound is $\pi$-$C_5H_5Mo(CO)_6Mo\pi$-$C_5H_5$. The reason for the different stoichiometry found previously is not clear, and it may be noted that the infra-red spectrum of the original sample in the solid state showed a definite splitting in the C-O stretching region which was not found in $C_5H_5W(CO)_6WC_5H_5$[15]. The present failure to repeat the original work and the formation of only $\pi$-$C_5H_5Mo(CO)_6Mo\pi$-$C_5H_5$ by the high-temperature reaction of cyclopentadiene with molybdenum carbonyl with properties and infra-red spectrum identical to those of the product formed by air oxidation of $\pi$-$C_5H_5Mo(CO)_3H$, strongly suggests that the original stoichiometry was incorrect.

The infra-red spectrum of $\pi$-$C_5H_5Mo(CO)_6Mo\pi$-$C_5H_5$ is almost identical with that of its tungsten analogue both in solution and in the solid state; in the C-O stretching region it has strong bands at 1960 and 1916 $cm^{-1}$ in solution and at 1951, 1920, and 1892 $cm^{-1}$ in the solid state.

[14] G. WILKINSON *J. Amer. Chem. Soc.* **76**, 209 (1954).
[15] F. A. COTTON, A. D. LIEHR, and G. WILKINSON *J. Inorg. Nucl. Chem.* **1**, 175 (1955).

TABLE 4.—INFRA-RED SPECTRA*

| Compound | Column | Compound | Column |
|---|---|---|---|
| $\pi$-$C_5H_5Cr(NO)_2CH_3$ | 1 | $\pi$-$C_5H_5Mo(CO)_2C_2H_5$ | 12 |
| $\pi$-$C_5H_5Cr(NO)_2C_2H_5$ | 2 | $\pi$-$C_5H_5Mo(CO)_2$iso-$C_3H_7$ | 13 |
| $\pi$-$C_5H_5Cr(NO)_2CH_2Cl$ | 3 | $\pi$-$C_5H_5W(CO)_3CH_3$ | 14 |
| $\pi$-$C_5H_5Cr(NO)_2C_6H_5$ | 4 | $\pi$-$C_5H_5W(CO)_2C_2H_5$ | 15 |
| $\pi$-$C_5H_5Cr(NO)_2\sigma C_5H_5$ | 5 | $(\pi$-$C_5H_5)_2Ti(CH_3)_2$ | 16 |
| $\pi$-$C_5H_5Cr(CO)_3CH_3$ | 6 | $\pi$-$C_5H_5Mo(CO)_2H$ | 17 |
| $\pi$-$C_5H_5Fe(CO)_2CH_3$ | 7 | $\pi$-$C_5H_5W(CO)_3H$ | 18 |
| $\pi$-$C_5H_5Fe(CO)_2C_2H_5$ | 8 | $\pi$-$C_5H_5Mo(CO)_2NO$ | 19 |
| $\pi$-$C_5H_5Fe(CO)_2C_6H_5$ | 9 | $\pi$-$C_5H_5Mo(CO)_2Cl$ | 20 |
| $\pi$-$C_5H_5Fe(CO)_2\sigma C_5H_5$ | 10 | $\pi$-$C_5H_5Mo(CO)_2Br$ | 21 |
| $\pi$-$C_5H_5Mo(CO)_2CH_2$ | 11 | $\pi$-$C_5H_5Mo(CO)_2I$ | 22 |

* The spectra were measured in solution in $CCl_4$, 4000–1350 $cm^{-1}$, and in $CS_2$, 1350–450 $cm^{-1}$, except for the compounds 6, 16, 17, 18, and 19, which were measured in $CS_2$ solution only.

TABLE 4 (continued)

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| C-O, N-O overtone | 3530 *w*<br>3410 *m*<br>3330 *w* | 3530 *w*<br>3410 *m*<br>3330 *w* | 3550 *w*<br>3430 *m*<br>3330 *w* | 3530 *w*<br>3430 *m*<br>3330 *w* | 3530 *vw*<br>3410 *w*<br>3330 *vw* | | 3900 *w* |
| C-H stretch | 3105 *w*<br>2958 *m*<br>2889 *m* | 3105 *w*<br>2920 *ms*<br>2840 *m* | 3100 *w*<br>2960 *sh*<br>2910 *m*<br>2270 *w* | 3100 *w*<br>3030 *m* | 3080 *m*<br>2952 *w* | 3085 *w*<br>2950 *m*<br>2870 *m* | 3105 *w*<br>2960 *m*<br>2900 *m*<br>2810 *w* |
| C-O, N-O stretch | 1779 *vs*<br>1670 *vs* | 1777 *vs*<br>1673 *vs* | 1797 *vs*<br>1704 *vs* | 1820 *sh*<br>1790 *vs*<br>1718 *sh*<br>1685 *vs* | 1787 *vs*<br>1685 *vs* | 2010 *vs*<br>1930 *vs* | 2120 *w*<br>2010 *vs*<br>1955 *vs*<br>1920 *w* |
| | | | | 1560 *m* | 1610 *w* | | |
| | | | | 1485 *w* | | | 1840 *w* |
| | | | | 1470 *ms* | | | 1760 *w* |
| | | 1450 *m* | 1430 *sh* | 1450 *w* | 1445 *m* | | 1680 *w* |
| | 1430 *m* | 1430 *m* | 1425 *m* | 1425 *ms* | 1430 *m* | | 1520 *w* |
| | 1360 *w* | 1370 *m* | 1360 *w* | | 1375 *m* | | 1430 *m* |
| | | | 1300 *w* | | 1360 *w* | | 1420 *m* |
| | 1130 *ms* | 1125 *ms* | 1115 *vs* | 1150 *w* | | 1160 *m* | 1360 *w* |
| | | | | | 1085 *w* | | |
| | 1060 *w* | | 1085 *w* | 1055 *m* | 1080 *m* | | |
| | | | 1060 *w* | 1065 *w* | 1060 *w* | | 1170 *s* |
| | 1015 *m* | 1013 *sh* | 1015 *m* | 1010 *ms* | 1020 *ms* | 1010 *m* | 1110 *m* |
| | 1010 *m* | 1006 *m* | 1005 *m* | | 1005 *m* | | |
| | | | | | 965 *m* | | |
| | | | | | 930 *w* | | 1060 *w* |
| | 915 *w* | | 920 *w* | 995 *m* | 920 *sh* | | 1015 *m* |
| | | | | | 885 *m* | | 1000 *m* |
| | | | | | 840 *s* | 848 *sh* | |
| | 820 *vs* | 815 *vs* | 825 *vs* | 820 *vs* | 825 *vs* | 832 *s* | |
| | 744 *w* | | 760 *w* | 772 *m* | 805 *w* | 650 *s* | 920 *w* |
| | 730 *sh* | | 700 *w* | 726 *vs* | 740 *vs* | | |
| | 646 *m* | | 670 *vs* | 695 *s* | 735 *sh* | | 840 *sh* |
| | 604 *vs* | | | 688 *m* | 707 *w* | | 825 *vs* |
| | 579 *m* | | | | | | 790 *m* |
| | 534 *w* | | | | | | 760 *vw* |
| | | | | | | | 634 *s* |
| | | | | | | | 592 *s* |
| | | | | | | | 570 *s* |
| | | | | | | | 560 *s* |
| | | | | | | | 466 *w* |



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TABLE 4 (continued)

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|
| C-O, N-O overtone | 3900 *w* | 3900 *w* | 3920 *w* | 4000 *vw*<br>3900 *w*<br>3820 *vw* | 4000 *vw*<br>3900 *w*<br>3820 *vw* | | 4000 *vw*<br>3900 *vw*<br>3820 *vw* |
| C-H stretch | 3100 *w*<br>2910 *s*<br>2840 *m* | 3105 *w*<br>3040 *m* | 3080 *m*<br>2907 *w* | 3110 *w*<br>2990 *m*<br>2910 *m*<br>2820 *w* | 3110 *w*<br>2942 *ms*<br>2863 *m* | 3100 *w*<br>2930 *s*<br>2840 *m* | 3105 *w*<br>2960 *m*<br>2870 *m*<br>2810 *w* |
| C-O, N-O stretch | 2120 *w*<br>2010 *vs*<br>1950 *vs*<br>1920 *w* | 2020 *vs*<br>1960 *vs*<br>1930 *m* | 2013 *vs*<br>1965 *vs* | 2020 *vs*<br>1937 *vs* | 2016 *vs*<br>1932 *vs* | 2010 *vs*<br>1930 *vs* | 2020 *vs*<br>1930 *vs*<br>1740 *w* |
| | 1830 *w*<br>1760 *w*<br>1720 *w*<br>1680 *w*<br>1450 *s*<br>1430 *m*<br>1420 *m*<br>1370 *m*<br><br><br>1150 *vs*<br>1115 *m*<br><br>1055 *m*<br><br>1015 *ms*<br>1000 *ms*<br>965 *m*<br>930 *w*<br>915 *w*<br><br>845 *m*<br>825 *vs*<br>694 *w* | <br><br><br>1570 *s*<br>1470 *s*<br>1430 *m*<br>1420 *m*<br>1360 *w*<br><br><br><br>1060 *m*<br>1050 *m*<br><br>1010 *s*<br>995 *m*<br><br><br><br>840 *sh*<br>828 *s*<br>760 *w*<br>728 *vs*<br>695 *s*<br>675 *w* | 1780 *w*<br>1690 *w*<br>1620 *w*<br>1450 *ms*<br>1430 *m*<br>1420 *sh*<br>1375 *m*<br>1360 *w*<br><br>1110 *w*<br>1105 *w*<br>1090 *m*<br>1080 *w*<br>1050 *w*<br>1015 *ms*<br>1000 *ms*<br>960 *w*<br>890 *ms*<br><br>860 *ms*<br>840 *sh*<br>830 *s*<br>810 *w*<br>747 *vs*<br>740 *vs*<br>710 *m* | <br><br>1515 *w*<br><br><br>1420 *m*<br>1355 *w*<br><br><br>1167 *m*<br>1110 *w*<br><br><br>1060 *w*<br>1010 *m*<br>1005 *m*<br><br><br><br>810 *vs* | <br><br><br><br>1450 *m*<br>1420 *m*<br>1370 *m*<br><br>1220 *w*<br>1140 *s*<br>1110 *w*<br><br><br>1060 *w*<br>1010 *m*<br>1005 *sh*<br><br>965 *m*<br>910 *w*<br>830 *sh*<br>810 *vs* | 1455 *m*<br>1445 *m*<br>1430 *sh*<br>1420 *m*<br>1360 *w*<br>1220 *w*<br>1137 *s*<br>1128 *s*<br>1088 *m*<br><br>1010 *m*<br>1005 *m*<br><br><br>808 *vs* | <br><br>1425 *m*<br>1350 *w*<br><br><br>1185 *m*<br>1110 *w*<br>1060 *w*<br>1030 *w*<br>1010 *m*<br>1005 *sh*<br>920 *w*<br><br>840 *sh*<br>820 *vs*<br>775 *w* |

## 2.16. *High-resolution Nuclear Magnetic Resonance Spectra*

Spectra were obtained, using a Varian Associates high-resolution n.m.r. spectrometer, Model V4300A, with a crystal-controlled radio frequency of 40 megacycles. The samples were carefully purified from paramagnetic impurities, the presence of which leads to loss of radio-frequency power by leakage in the coils and also to reduction in the relaxation time, with consequent reduction in the signals. The samples were sealed in vacuum in 5-mm-diameter Pyrex tubes.

The position of the phenyl proton resonance and the separation of the phenyl and methyl proton resonances in toluene were used as references for the measurements; for this separation a value of 5·13 p.p.m. was assumed.[16] The chemical shifts with reference to water can be calculated from our data by assuming a chemical shift for the phenyl-group protons in toluene of −1·77 p.p.m. relative to water. The data are accurate to ±5%.

Where possible, samples were run in carbon disulphide or benzene solution to show that no proton resonances due to the sample occurred in the toluene region. Subsequently, toluene was used as a solvent, except where noted. In the case of $H_2Fe(CO)_4$, a sealed capillary containing toluene was

[16] B. P. DAILEY and J. N. SHOOLERY *J. Amer. Chem. Soc.* **77**, 3977 (1955).

TABLE 4 (continued)

| | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|---|
| C-O, N-O overtone | 4000 *vw*<br>3900 *w*<br>3820 *vw* | | 4000 *vw*<br>3960 *w*<br>3860 *vw* | 4000 *vw*<br>3950 *w*<br>3850 *vw* | 4010 *vw*<br>3920 *w*<br>3330 *m* | | | |
| C-H stretch | 3090 *w*<br>2930 *m*<br>2850 *m* | 3090 *w*<br>2930 *m*<br>2860 *m*<br>2780 *w* | 3105 *w* | 3100 *w* | 3110 *w* | 3100 *w* | | 3100 *w* |
| C-O, N-O stretch | 2020 *vs*<br>1920 *vs* | | 2030 *vs*<br>1949 *vs*<br>1913 *w* | 2020 *vs*<br>1929 *vs*<br>1980 *w* | 2015 *vs*<br>1940 *vs*<br>1910 *w*<br>1678 *vs* | 2055 *vs*<br>1980 *vs*<br>1960 *vs* | 2049 *vs*<br>1977 *vs*<br>1958 *vs* | 2040 *vs*<br>1968 *vs*<br>1955 *sh* |
| | | | 1790 *w*<br>1730 *w* | 1840 *w*<br>1710 *w* | | 1430 *sh*<br>1420 *m* | | 1420 *m* |
| | | 1820 *w*<br>1720 *w* | | | 1350 *w*<br>1105 *w* | 1360 *w* | | 1360 *w* |
| | 1450 *m* | 1630 *w* | | | 1090 *w* | | | |
| | 1420 *m* | | | | 1050 *w* | 1010 *m* | | 1010 *m* |
| | 1370 *m* | 1365 *w* | 1355 *w* | 1350 *w* | 1005 *s* | 1005 *sh* | | 1005 *sh* |
| | | | | | 896 *m* | 855 *w* | | 855 *w* |
| | 1235 *w* | 1150 *w* | 1270 *w* | 1210 *w* | 830 *sh* | 815 *vs* | | 815 *vs* |
| | 1160 *s* | 1117 *sh* | 1150 *w* | 1150 *w* | 800 *vs* | | | 570 *vs* |
| | 1110 *w* | 1103 *m* | 1110 *w* | | | | | 526 *s* |
| | 1060 *w* | 1065 *w* | 1060 *w* | 1055 *w* | | | | 474 *s* |
| | 1030 *w* | | | | | | | |
| | 1010 *m* | 1018 *ms* | 1005 *m* | 1005 *m* | | | | |
| | 1005 *sh* | | | | | | | |
| | 965 *m* | 910 *w* | 975 *w* | | | | | |
| | 910 *w* | 905 *w* | 905 *w* | | | | | |
| | 840 *sh* | | | | | | | |
| | 815 *vs* | 810 *vs* | 815 *s* | 817 *s* | | | | |
| | | 730 *w* | | | | | | |

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inserted inside the n.m.r. sample tube in order to provide "internal" reference points. The procedure of sample replacement was thus avoided and errors due to changes in the field minimized.

The n.m.r. data are presented in Table 5; in addition to the compounds described in this paper, several other compounds were run and the data of other authors quoted for comparison. The areas under the peaks were not accurately measured, except where noted, but the relative sizes of the peaks for compounds with more than one type of hydrogen appeared to be appropriate. In an earlier note[17] we have reported the n.m.r. spectrum of $(C_5H_5)_2ReH$, which had been measured for us in another laboratory using the method of sample replacement. We have now repeated the measurement in this laboratory in toluene solution and obtained more reliable data which may be found in Table 5.

Since comparatively concentrated solutions (10% by weight or more) are often required for n.m.r. studies, the measurements necessarily had to be limited to those compounds with sufficiently high solubilities in organic solvents. The compound $(C_5H_5)_2Mn_2(NO)_3$[2] which would have been particularly interesting to study, was not sufficiently soluble in organic solvents.

## 2.17. *Ultra-violet Absorption Spectra*

The spectra were measured in cyclohexane solution, using a Cary recording spectrophotometer with quartz cells. In addition to the maxima which may be found in Table 6, all of the spectra showed very intense absorptions increasing with decreasing wavelength; at 2400 Å, $\varepsilon = 10{,}000$–$25{,}000$.

[17] G. WILKINSON and J. M. BIRMINGHAM *J. Amer. Chem. Soc.* **77**, 3421 (1955).

TABLE 5.—NUCLEAR MAGNETIC RESONANCE SPECTRA

| Compound | Chemical shift in p.p.m. vs. $C_6H_6$ protons in toluene | | | | | |
|---|---|---|---|---|---|---|
| | $\sigma$-$C_5H_5$ | $\pi$-$C_5H_5$ | $CH_3$ | $C_6H_5$ | H | Misc. |
| $(\pi\text{-}C_5H_5)_2Fe$ | — | 3·1 | — | — | — | — |
| $(\pi\text{-}C_5H_5)_2Ru$ | — | 2·7 | — | — | — | — |
| $(\pi\text{-}C_5H_4CH_3)_2Fe$[a] | — | 3·2 | 5·4 | — | — | — |
| $\pi\text{-}C_5H_5Mn(CO)_3$ | — | 3·1 | — | — | — | — |
| $\pi\text{-}C_5H_5NiNO$ | — | 2·2 | — | — | — | — |
| $\pi\text{-}C_5H_5Cr(NO)_2CH_3$ | — | 2·6 | 6·9 | — | — | — |
| $\pi\text{-}C_5H_5Mo(CO)_3CH_3$ | — | 2.6 | 6·9 | — | — | — |
| $\pi\text{-}C_5H_5Mo(CO)_3C_2H_5$ | — | 2·5 | — | 6·0[b] | — | — |
| $\pi\text{-}C_5H_5Mo(CO)_3iso\text{-}C_3H_7$ | — | 2·5 | 5·5 | — | — | — |
| | — | — | 6·0[c] | — | — | — |
| $\pi\text{-}C_5H_5W(CO)_3CH_3$ | — | 2·5 | 7·0 | — | — | — |
| $\pi\text{-}C_5H_5W(CO)_3C_2H_5$ | — | 2·5 | — | 5·8[b] | — | — |
| $\pi\text{-}C_5H_5Fe(CO)_2CH_3$ | — | 3·0 | 7·2 | — | — | — |
| $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ | — | 1·5 | 7·6 | — | — | — |
| $\pi\text{-}C_5H_5Fe(CO)_2\sigma\text{-}C_3H_5$[d] | 0·6 | 2·1 | — | — | — | — |
| $\pi\text{-}C_5H_5Cr(NO)_2\sigma\text{-}C_3H_5$[d] | 0·5 | 1·8 | — | — | — | — |
| $\sigma\text{-}C_5H_5CuP(C_2H_5)_3$ | 1·0 | — | — | 6·6[b] | — | — |
| $P(C_2H_5)_3$ | — | — | — | 6·4[b] | — | — |
| $(C_5H_5)_2Mg$[e] | — | — | — | — | — | 0·3 |
| $(C_5H_5)_2Mg$[f] | — | — | — | — | — | 1·3 |
| $(\sigma\text{-}C_5H_5)_2Hg$ | 1·5[g] | — | — | — | — | — |
| $(CH_3)_6Si_2O$ | — | — | 7·4 | — | — | — |
| $C_5H_6$ | — | — | — | — | — | 0·8[h]<br>4·2[i] |
| $\pi\text{-}C_5H_5Cr(CO)_3H$ | — | 3·1 | — | — | 13·1 | — |
| $\pi\text{-}C_5H_5Mo(CO)_3H$ | — | 2·5 | — | — | 12·8 | — |
| $\pi\text{-}C_5H_5W(CO)_3H$ | — | 2·4 | — | — | 14·7 | — |
| $(\pi\text{-}C_5H_5)_2ReH$ | — | 3·1 | — | — | 20·5 | — |
| $(C_2H_5)_3SiH$[j] | — | — | — | 6·2[b] | 3·2 | — |
| $H_2Fe(CO)_4$[k] | — | — | — | — | 17·4 | — |
| $HCo(CO)_4$[l] | — | — | — | — | 17·3 ± 2 | — |

[a] L. T. REYNOLDS and G. WILKINSON, unpublished work.
[b] Methylene and methyl group resonances not resolved.
[c] Methyl peak split by methylene hydrogen; methylene peak was not resolved.
[d] In $CS_2$ solutions (by sample replacement): area ratio 4·9($\sigma$): 5·0($\pi$).
[e] Probably ionic (cf. reference 12).
[f] In tetrahydrofuran solution.
[g] Broad shoulder at about 1·8 p.p.m.
[h] Olefinic protons.
[i] Methylenic protons
[j] A. LOUIS ALLRED, private communication.
[k] G. WILKINSON and F. A. COTTON, unpublished work; no solvent used.
[l] Calculated from data of H. S. GUTOWSKY.[18]

[18] H. S. GUTOWSKY, quoted by R. A. FRIEDEL, I. WENDER, S. L. SHUFLER, and HEINZ W. STERNBERG, *J. Amer. Chem. Soc.* **77**, 3951 (1955).

TABLE 6—ULTRA-VIOLET ABSORPTION SPECTRA

| Compound | λ (Å) | $\varepsilon_{max}$ |
|---|---|---|
| $\pi$-$C_5H_5Mn(CO)_3$ | 3,320 | 1,010 |
| $\pi$-$C_5H_5Cr(NO)_2CH_3$ | 4,600 | 1,520 |
| | 3,000 | 2,750 |
| $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$ | 4,500 | 1,360 (shoulder) |
| | 3,040 | 11,300 |
| $\pi$-$C_5H_5Mo(CO)_3CH_3$ | 3,150 | 1,960 |
| $\pi$-$C_5H_5Mo(CO)_3C_2H_5$ | 3,130 | 2,120 |
| $\pi$-$C_5H_5W(CO)_3CH_3$ | 3,130 | 2,430 |
| $\pi$-$C_5H_5W(CO)_3C_2H_5$ | 3,130 | 2,390 |
| $\pi$-$C_5H_5Fe(CO)_2CH_3$ | 3,530 | 730 |
| $\pi$-$C_5H_5Fe(CO)_2\sigma$-$C_5H_5$ | 3,180 | 8,040 |
| $(C_5H_5)_2Mn_2(NO)_3$ | 2,930 | 24,000 |

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### 2.18. *Infra-red Spectra*

Infra-red spectra were measured on a Perkin-Elmer double-beam recording spectrophotometer, Model 21, using sodium-chloride optics. In the potassium-bromide region, a Perkin-Elmer single-beam spectrometer, Model 12c, was used.

Most of the compounds were studied in carbon-tetrachloride solution from 4000 $cm^{-1}$ to 1350 $cm^{-1}$ and in carbon disulphide from 1350 $cm^{-1}$ to 450 $cm^{-1}$. The data are presented in Table 4. In addition, the spectrum of the vapour of $C_5H_5Mo(CO)_3CH_3$ was obtained at about 100°C: in this case, the bands in the C-O stretching region occurred at 2030 $cm^{-1}$ (s), 1957 $cm^{-1}$ (vs), and 1920 $cm^{-1}$ (w). The methyl group is identified by its two C-H stretching frequencies at ~2960 $cm^{-1}$ and 2890 $cm^{-1}$, and by symmetrical metal-methyl deformation frequency at ~1150 $cm^{-1}$. The ethyl group is identified by its $C-CH_3$ asymmetric deformation at ~1450 $cm^{-1}$ and by its $C-CH_3$ symmetric deformation at ~1370 $cm^{-1}$. For phenyl compounds, C-C stretching frequencies are found at ~1570 $cm^{-1}$ and ~1470 $cm^{-1}$ (the C-C stretching frequency for the π-cyclopentadienyl ring lies in the region 1430–1420 $cm^{-1}$); the C-H out-of-plane bending vibrations characteristic of monosubstituted benzenes are found at 728 and 695 $cm^{-1}$.

## 3. DISCUSSION

### 3.1. *The Structure of the Alkyl and Aryl Derivatives*

In all the compounds $\pi$-$C_5H_5M(CO)_x(NO)_yR$, the cyclopentadienyl ring is unquestionably bound to the metal atom by a bond similar to that in ferrocene and other *bis*(π-cyclopentadienyl) metal compounds.[19, 20] For mononuclear π-cyclopentadienyl compounds this point has been previously discussed,[2] and a comparison of the infra-red absorption data in Table 4 with those given in previous papers[2] shows many common features attributable to the π-cyclopentadienyl ring-metal system. Additional proof of the π-cyclopentadienyl nature of the rings is the failure, e.g. of $\pi$-$C_5H_5Cr(NO)_2CH_3$ or $\pi$-$C_5H_5W(CO)_3C_2H_5$, to react with maleic anhydride in benzene solution, with water, or with ferrous chloride in tetrahydrofuran. For the compound $(\pi$-$C_5H_5)_2Ti(CH_3)_2$, the same arguments concerning the bonding of the rings hold. In the compounds such as $\pi$-$C_5H_5Cr(NO)_2\sigma$-$C_5H_5$, there is unequivocal evidence, which is discussed in detail below, that there is only one π-cyclopentadienyl

[19] W. MOFFITT *J. Amer. Chem. Soc.* **76**, 3386 (1954).
[20] J. D. DUNITZ and L. E. ORGEL *J. Chem. Phys.* **23**, 954 (1955).

ring bonded to the metal atom. At first sight, it might appear certain from the methods of preparation of the alkyl and aryl compounds, and from the diamagnetism of the molecules (which is to be expected since these are structurally similar to other mononuclear $\pi$-cyclopentadienyl metal compounds[2]), that the alkyl and aryl groups in $\pi$-$C_5H_5M(CO)_x(NO)_yR$ are indeed bound directly to the transition-metal atom. It is conceivable, however, although unlikely (since feasible electronic structures would be difficult to write), that the alkyl or aryl groups could be attached to nitrogen, carbon, or oxygen atoms, e.g. as an ether grouping M—C—O—R. There is strong evidence that this is not the case. (a) In the compounds $\pi$-$C_5H_5Cr(NO)_2R$ and $\pi$-$C_5H_5Fe(CO)_2R$, two intense N-O or C-O stretching frequencies are observed in essentially the same regions and with essentially the same separations, e.g. for the N-O bands, $\sim$100 $cm^{-1}$, as when alkyl or aryl groups are absent; thus the bands in $\pi$-$C_5H_5Fe(CO)_2CH_3$ are at 2010 and 1955 $cm^{-1}$, whereas in $\pi$-$C_5H_5Co(CO)_2$ they are at 2028 and 1967 $cm^{-1}$ and in $\pi$-$C_5H_5Fe(CO)_2Cl$ at 2050 and 2010 $cm^{-1}$. (*b*) Catalytic hydrogenation of $\pi$-$C_5H_5Cr(NO)_2CH_3$ in ethanol solution at 25°C, using ADAMS's catalyst, gave methane, which was identified by its infra-red spectrum. No methylamine, which would have been expected from an N-methyl compound, could be detected; an O-methyl compound would not be reduced to methane under these conditions. (c) In the $\pi$-$C_5H_5M(CO)_3R$ alkyl compounds, the existence of only two strong bands in the 1900–2000 $cm^{-1}$ region (*vide infra*) and the occurrence of a medium to strong band in the region 1110–1190 $cm^{-1}$, might be construed as indicating two M-C-O groups and one M-C-O-R group in the molecule. Analogies to carbon compounds, where in ethers, for example, O-$CH_3$ stretches occur at 1150–1060 $cm^{-1}$ (s) and an O-$CH_3$ deformation in $CH_3COCH_3$ at 1466 $cm^{-1}$, may well be invalid, and there seem to be too few bands to fit this possibility. The medium-strong band in the 1110–1190 $cm^{-1}$ region occurs also in $\pi$-$C_5H_5Cr(NO)_2R_{alkyl}$ and $\pi$-$C_5H_5Fe(CO)_2R_{alkyl}$ e.g. in $\pi$-$C_5H_5Cr(NO)_2CH_3$ at 1130 $cm^{-1}$, and is hence probably attributable to metal-alkyl group interaction; it may be noted that in dimethylzinc[21] the symmetrical metal-methyl deformation frequency occurs in this region. (d) In the methyl compounds $\pi$-$C_5H_5M(CO)_x(NO)_yCH_3$, the methyl-group proton resonances (Table 5) all occur at a similarly large shift relative to methyl groups in benzene derivatives or in 1,1′dimethylferrocene, and resemble in this respect methyl groups in methyl silicon compounds (Table 5 and ref. 22); furthermore, in the ethyl compounds in no case are the methyl and methylene proton resonances resolved. The similarity of the chemical shifts in the $\pi$-$C_5H_5M(CO)_2R$ compounds, where any possibility of bonding of the alkyl group other than directly to the metal atom is clearly ruled out as above, to those in the $\pi$-$C_5H_5M(CO)_3R$ compounds indicates similar bonding for the alkyl groups in all cases.

In view of the above, we take it that in the $\pi$-$C_5H_5M(CO)_x(NO)_2R$ compounds there is a metal-to-carbon $\sigma$-bond. Whilst it is clear that metal-to-carbon $\sigma$-bonds, as in simple alkyls and aryls, are unstable for most of the transitional metals (cf. ref. 1a), it now seems that the presence on the metal atom of a $\pi$-cyclopentadienyl ring, together with other suitable ligands, so changes the orbitals remaining for bonding purposes that stable $\sigma$-bonds can be formed between a transitional metal atom and an alkyl or aryl group.

[21] Cf. H. S. GUTOWSKY *J. Chem. Phys.* **17**, 129 (1949).
[22] Cf. Table 5 and also *Radiofrequency Spectroscopy* **1**, No. 2, Varian Associates, Palo Alto, Calif.

JAFFÉ[23] has made calculations concerning the stability of transition metal-to-carbon σ-bonds in simple alkyls or aryls, i.e. with no other groups present on the metal atom, based on $sd^n$ hybrids of the metal atom; he concluded that the bonds would have low stability and that the strength should be greatest for elements of the first transitional series. Aside from considerations of bond strength in cases such as those JAFFÉ considered, the failure to isolate simple alkyls and aryls may be attributed in part to the fact that partially occupied *d* orbitals would be present which would be expected to lead to increased lability and reactivity. The compounds noted in the present work are all diamagnetic, and the chemical reactivity would be expected to be lower for this reason alone, quite apart from other factors.

In the previous discussion of the fact that the mononuclear π-cyclopentadienyl carbon-monoxide or nitric-oxide metal derivatives follow a "fourteen-electron rule",[2] it was suggested that in considering the bonding of the ligands to the metal atom it was not necessary to invoke the use of more than one *p* orbital, on the average, together with *s* and *d* orbitals; in the first transitional series, the *p* orbitals lie considerably above those of the *s* and *d* orbitals, and thus on energetic grounds alone their use in bonding would be disfavoured.

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In the bonding of an alkyl group to the metal atom, there is small possibility of multiple bonding between the metal and the carbon atoms. This is in contrast to the case where carbon monoxide is bound to a metal atom, since here, where there are orbitals available on the ligand, multiple bonds to the metal are well known to occur. Thus, in order to obtain a stable metal-to-carbon σ-bond, the use of a strongly directed orbital of the metal atom is much more necessary than is required for bonding ligands of the type of carbon monoxide. It is not possible to get strongly directed orbitals using only *s* and *d* hybrids, since from symmetry arguments the resulting orbitals must be gerade, i.e. the electron density will be as great in the direction pointing away from the ligand as in the direction towards it. Hence the formation of stable metal-to-carbon σ-bonds may be considered to require considerable *p* character in order to achieve the necessary directional property for good overlap with the orbitals of the carbon atom. Since the energy of the *p* orbitals relative to the *d* and *s* orbitals falls in going from the first to the third transitional-series elements, the participation of *p* orbitals in the bonding of the groups other than the π-cyclopentadienyl ring should become increasingly easy.

Although other factors may contribute to the chemical stabilities, the stability order does suggest that the strength of the metal-to-carbon σ bond increases with increasing atomic weight of the metal, as would be expected on the above view.

The structures of the molecules $\pi\text{-}C_5H_5M(CO)_x(NO)_yR$ must be similar to those of the other mononuclear π-cyclopentadienyl metal compounds.[2] For three groups, as in $\pi\text{-}C_5H_5Cr(NO)_2CH_3$, the NO and $CH_3$ groups will be directed towards the corners of a trigonal, not necessarily regular, pyramid with the metal at its apex. For the Group VI metal compounds, $\pi\text{-}C_5H_5M(CO)_3R$, the infra-red data concerning the C-O stretching frequencies suggest that there are two sets of compounds which normally would be expected to have a similar configuration, i.e. one with the CO and R groups directed to the corners of a tetragonal, not necessarily regular, pyramid. For the compounds where R = H, $CH_3$, $C_2H_5$, and *iso*-$C_3H_7$, two strong absorptions occur in

[23] (a) H. H. JAFFÉ and G. O. DOAK *J. Chem. Phys.* **21**, 19b (1953).
(b) H. H. JAFFÉ *ibid.* **22**, 1462 (1954).

the C-O stretching region. It would be tempting to assume that the CO groups have local symmetry $C_{3v}$, with the R groups lying along the principal axis of the molecule; in the case of the hydrides this may well be so (*vide infra*). When R = Cl, Br, and I, three bands are found, one of these appearing as a shoulder in the iodide, with the splitting increasing in the order I<Br<Cl. In the vapour-phase spectrum of $\pi$-$C_5H_5Mo(CO)_3CH_3$, and often in the solution spectra of the first group of compounds, a third band does occur in the C-O stretching region, but of intensity so low that it is not certain that it is a fundamental. The existence of only two strong bands in the first group may hence be due to accidental cancellation of dipole moments, or to the coincidence of two bands; the latter explanation gains support from the decreasing splitting in the halides with decreasing electro-negativity of the R group.

### 3.2. *σ-Bonded Cyclopentadienyl Derivatives*

The chemical properties of cyclopentadienyltrimethylsilane[24] indicated that the cyclopentadienyl ring was bonded to the silicon atom by a localized silicon-to-carbon bond. The first evidence that similar bonds could be formed between the $C_5H_5$ ring and a transitional metal came from a study of the compounds $(C_5H_5)_3Mn_2(NO)_3$[3] and $C_5H_5CuP(C_2H_5)_3$,[25] in which the compound $(C_5H_5)_2Hg$[25] was prepared for comparison. It was subsequently suggested[6] that in the compounds of empirical formula, $(C_5H_5)_2Cr(NO)_2$ and $(C_5H_5)_2Fe(CO)_2$, one ring was $\sigma$-bonded to the metal atom.

The evidence that in these various compounds, one $C_5H_5$ ring (in the case of $(C_5H_5)_2Hg$, two rings) is bound to the metal atom by a localized bond is as follows. (a) All the compounds react with maleic anhydride, although the adducts have been characterized only in the cases of the silicon and mercury compounds. (b) Where the C-H stretching region could be investigated, the infra-red spectrum of the compounds showed a band at 3080 $cm^{-1}$(m) and one or two weaker absorptions. Cyclopentadiene itself shows C-H stretching frequencies in the infra-red at 3100 $cm^{-1}$ and 2900 $cm^{-2}$; a $\pi$-cyclopentadienyl ring, on the other hand, has but one frequency in this region at 3100–3085 $cm^{-1}$ (w). It may be noted that one of the bands from a $\sigma$-cyclopentadienyl ring may overlap the C-H frequency due to a $\pi$-cyclopentadienyl ring, so that in a compound with both types of ring present, more than two C-H stretching frequencies may not be found. In addition, the spectra of these compounds showed an absorption at 1610–1640 $cm^{-1}$ (w), possibly attributable to a C=C stretching frequency, and at least one absorption at 720–760 $cm^{-1}$ (vs). These bands are not observed in the spectra of $\pi$-cyclopentadienyl compounds (cf. ref. 2 and Table 4), but, as previously pointed out,[25] the spectra of the $\sigma$-cyclopentadienyl compounds of copper, mercury, and silicon otherwise bear little resemblance to one another. The compounds $(C_5H_5)_2Cr(NO)_2$, $(C_5H_5)_2Fe(CO)_2$, and $(C_5H_5)_3Mn_2(NO)_3$ have in common bands at 1445 (m), 1375 (m), 1085 (m), 885 (m), and 840 (s) $cm^{-1}$, none of which are due to the $\pi$-cyclopentadienyl ring. (c) In the ultra-violet absorption spectra of the compounds, intense end-absorption obscures the region where a diene system might be expected to absorb ($\varepsilon$ = 3000 at 2400 Å); however, as discussed previously,[25] the mercury and copper compounds have intense absorptions which are probably due to the metal-carbon

[24] K. C. FRISCH *J. Amer. Chem. Soc.* **75**, 6050 (1953).
[25] T. S. PIPER and G. WILKINSON *J. Inorg Nucl. Chem.* **2**, 32 (1956).

σ-bond. (d) The high-resolution nuclear magnetic-resonance spectra of $(C_5H_5)_2Cr(NO)_2$ and $(C_5H_5)_2Fe(CO)_2$ show two peaks whose chemical shifts are appropriate for a σ-bonded and a π-bonded ring, respectively, and provide unequivocal evidence for the existence of two types of cyclopentadienyl rings in the compounds. For $(C_5H_5)_2Hg$ and $C_5H_5CuP(C_2H_5)_3$, peaks characteristic of σ-cyclopentadienyl rings are also observed. These points are discussed in detail below.

### 3.3. *High-resolution Nuclear Magnetic Resonance (n.m.r.) Studies*

Table 5 records the n.m.r. spectra of several of the compounds prepared in this work. Some general features are apparent. All of the compounds which, from other physical and chemical evidence, are known to have a π-cyclopentadienyl ring bonded to the transition-metal atom, have a single proton resonance between 2·5 and 3·1 p.p.m. relative to benzene; for magnesium cyclopentadienide, the shift is very solvent-dependent, but both here and in the σ-cyclopentadienides the proton shift is considerably smaller than for π-cyclopentadienyl compounds. For all of the compounds with a metal-methyl bond, the methyl-group protons show a peak ~7 p.p.m.; in the ethyl compounds, the methylene and methyl resonances were not resolved.

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The large chemical shifts of the "hydridic" hydrogen atoms in the chromium, molybdenum, and tungsten compounds $\pi\text{-}C_5H_5M(CO)_3H$ are similar to those observed for the compound $(\pi\text{-}C_5H_5)_2ReH$,[17] cobalt hydrocarbonyl,[18] and iron hydrocarbonyl. For these transitional metal "hydrides," which are certainly not hydrides in the sense of furnishing hydride ions, there is no obvious connection between acidity and the chemical shift. Thus, $(\pi\text{-}C_5H_5)_2ReH$ is a weak base, reacting with acids to form the cation $[(\pi\text{-}C_5H_5)_2ReH_2]^+$, the Group VI compounds are acids weaker than acetic acid, whilst the iron and cobalt hydrocarbonyls are well known to behave as strong acids in aqueous solution. The chemical shift of the "hydridic" protons falls in the order ReH > Co, FeH > Cr, Mo, or WH. Although the shift in the Cr, Mo, and W compounds is essentially the same, indicating the similar nature of the proton shielding, there is a very pronounced increase in chemical and thermal stability with increasing atomic weight—thus the tungsten compound is stable to about 180°C. A similar increase in stability with atomic weight might well occur with the simple hydrocarbonyls, but those of second or third series transitional elements can hardly be said to have been characterized at the present time. In these transitional metal "hydrides," the protons are extremely well shielded from the effects of the applied field; the chemical shifts, of 12–21 p.p.m. relative to benzene, are the largest recorded for protons, and are in striking contrast to the shifts for protons in normal hydrides, e.g. 3·2 p.p.m. for $(C_2H_5)_3SiH$. It would appear that the shifts cannot be attributed primarily to *s* electrons about the hydrogen nucleus, and the proton must be buried in the electron density surrounding the metal atom. The hydrogen atom may perhaps best be regarded as bound to *d* orbitals, nonbonding as far as other ligands are concerned. For the hydrocarbonyls the proton may be located between the ligands at about the same distance from the metal atom as the centroid of maximum charge for the metal-carbon bond of the ligands. For the π-cyclopentadienyl compounds the proton could also be located between the ring and the metal atom, e.g. in $(\pi\text{-}C_5H_5)_2ReH$ in the $d(a_1g)$ orbital; in the compounds with one π-cyclopentadienyl ring, location between the CO ligands and the ring are both possible positions.

In the various compounds where the methyl group is bound to the metal atom, absorptions are found at ~7 p.p.m. relative to benzene; these shifts for the methyl group are greater than is found for methyls attached to carbon atoms, e.g. as in toluene or 1,1′dimethylferrocene, but comparable to those observed for methyl silicon compounds, and may be due to the lower electronegativity of the atom to which carbon is bound. The nonresolution of the methyl and methylene proton resonances in both transition metal, silicon, and phosphorous ethyl compounds may have a similar explanation. DAILEY and SHOOLERY[16] have studied the electron withdrawal power of substituent groups in ethyl derivatives. Although in these cases the substituents formed bonds with the methylene group using primarily a *p* orbital, and hence analogy to the present cases where the involvement of *d* orbitals is possible may not necessarily be close, it would appear that where the electronegativity of the atom to which the methylene group is bound has an electronegativity value below ~1·7, the methyl and methylene resonances might be expected to coalesce. Whilst the different electronegativities of atoms to which a group is bound may be responsible for part of the chemical shifts, i.e. these results in part from variation in ionic character of the bonds, other factors are involved. Not only are the shifts, say for the methyl-group protons, larger when the group is bound to silicon or a transitional metal than when it is bonded to carbon, but in the $\pi$-cyclopentadienyl compounds the ring protons are considerably more diamagnetically shielded than those in benzene in spite of the well known chemical similarity of the $\pi$-cyclopentadienyl rings in ferrocene to that of benzene. Such a large diamagnetic shift could arise if the external field induces within these magnetically anisotropic molecules, a local secondary magnetic field which acts against the applied field at the proton positions. Electrons in *d* orbitals or in hybrid orbitals with *d* components may be involved, and directional effects due to the applied field might occur. In an analysis of the chemical shifts in fluorine compounds, SAIKA and SLICHTER[26] have concluded that paramagnetic terms for the atom were principally responsible for the chemical shifts; here, however, these led to a paramagnetic shift. In the present compounds, paramagnetic terms of atoms other than the one whose resonances are being studied may be important and their direction may be dependent on the geometry of the molecules. It seems safe to conclude that the unusually large diamagnetic shifts observed, e.g. for protons in the $\pi$-cyclopentadienyl or methyl groups, are due to the association with the metal atom.

Although it is not possible to say with any certainty, the greater stability of the methyl derivatives, compared to the ethyls, may be due to some double-bond character in the metal-to-carbon bond, since in organic chemistry it has been postulated that methyl groups can release electron density.[27] This might have been expected to decrease the electron density at the methyl-group protons; the shielding for the methyls is consistently greater than for the methyl + methylene protons in the ethyls, however, although if the metal-carbon distance were shorter in the methyl derivatives, increased shielding of the protons by electron density from other ligands or the metal atom might be expected.

For a $\sigma$-cyclopentadienyl ring, M— , we expected to observe two absorptions with areas in the ratio of 4 : 1 at chemical shifts of about +0·8 and +4·2 relative to

[26] A. SAIKA and C. P. SLICHTER *J. Chem. Phys.* **22**, 26 (1954).
[27] Cf. C. A. COULSON *Quarterly Reviews* **1**, 144 (1947).

benzene, characteristic of olefinic and methylenic hydrogens respectively. Cyclopentadiene itself shows such absorptions.

For the compounds noted above, for which other evidence indicates a σ-bonded cyclopentadienyl ring, only *one* peak could be attributed to this ring. For example, in the spectrum of $\pi$-$C_5H_5Fe(CO)_2\sigma$-$C_5H_5$, only two peaks were observed, at chemical shifts of +0·6 and +2·1 relative to benzene, with the area ratios of 1 : 1. The latter peak must be attributed to a π-cyclopentadienyl ring. One explanation of the fact that all the protons in σ-rings have the same chemical shift would be the dissociation of the compounds into ions, e.g. $\pi$-$C_5H_5Cr(NO)_2^+$, $\pi$-$C_5H_5Fe(CO)_2^+$, and $C_5H_5^-$; the failure of the compounds to react with water and ferrous chloride in tetrahydrofuran suggests that dissociation is unlikely; however, the compounds do react with acids and the possibility of a very slow reaction with water is not eliminated, since if the half time of the dissociated state is very short, reaction may occur only slowly. An alternative explanation is to postulate that the metal atom is executing a 1,2-rearrangement at a rate greater than the expected chemical shift of 200–300 cycles per second; the σ-cyclopentadienyl ring may thus be regarded as rotating, and in respect to n.m.r. measurements all of the protons thus become equivalent. Since mercury and some transition metals are known to form co-ordination complexes with unsaturated hydrocarbons, it is possible that the ring rotation occurs through an intramolecular complex of the metal atom with the π-electron system of the cyclopentadienyl ring as a transition state. Such a postulate is of course not inconsistent with infra-red and chemical evidence for a metal-carbon localized σ-bond, since the rotation undoubtedly would occur at a rate such that the metal atom is bound to a single carbon atom most of the time.

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### 3.4. *Grignard Reactions*

The products and the yields obtained in the synthesis of the metal alkyl and aryl derivatives by the Grignard method are given in Table 2. "Addition" refers to the formation of a metal-to-carbon bond and "reduction" to the formation of the known binuclear compounds, $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\pi\text{-}C_5H_5)_2Mo_2(CO)_6$. A careful search among the products formed by action of Grignard reagents on $\pi$-$C_5H_5Cr(NO)_2Br$ gave no evidence of a binuclear compound, although it might well be prepared by other methods. It should be noted that in each case considerable decomposition occurs with the formation of tars. The reactions leading to decomposition probably proceed similarly to the attack of Grignard reagents on the carbon-monoxide groups of metal carbonyls.[28]

From the table it may be seen that yields of addition are higher with diethyl ether than with tetrahydrofuran, with bromides and iodides than with chlorides, and with the methyl Grignard reagent than with ethyl or phenyl Grignard reagents. The yield of addition product may be explained in terms of the action of one mole of the Grignard reagent on a complex comprising one mole of the Grignard reagent with the cyclopentadienylmetal-halogen derivative, analogous to the mechanism postulated for the reaction of nitriles with Grignard reagents.[29] In agreement with this view, complex formation is decreased by a more polar solvent and by the more

[28] Cf. F. L. Benton, M. C. Noss, and P. A. McCusker *J. Amer. Chem. Soc.* **67**, 82 (1945).
[29] C. G. Swain *J. Amer. Chem. Soc.* **69**, 2306 (1947).

electronegative chloride ion leading to reduced yields of addition relative to reduction and decomposition. In the addition reaction, steric hindrance of the Grignard reagent in the case of ethyl or phenyl as compared to methyl, or of the metal atom in the case of $\pi$-$C_5H_5Mo(CO)_3I$ as compared to $\pi$-$C_5H_5Fe(CO)_2I$, may account for the observed yields. However, yield studies alone are hardly sufficient to determine the mechanism or mechanisms involved, and complex formation is suggested only as a convenient generalization. The reaction of sodium cyclopentadienide with $\pi$-$C_5H_5Cr(NO)_2Br$ and $\pi$-$C_5H_5Fe(CO)_2I$ produced the respective $\sigma$-cyclopentadienyl derivatives in 15–20% yield, but with $\pi$-$C_5H_5Mo(CO)_3I$ no derivative was obtained; no evidence for a molybdenum phenyl compound was obtained either. These results are perhaps related to the greater steric hindrance at the molybdenum atom and also to electronegativity differences, since while cations $[\pi\text{-}C_5H_5Cr(NO)_2]^+$ and $[\pi\text{-}C_5H_5Fe(CO)_2]^+$ have been characterized, a cationic species $[\pi\text{-}C_5H_5Mo(CO)_3]^+$ does not appear to exist.

. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 125 to 138. Pergamon Press Ltd., London

# UNTERSUCHUNGEN AN HETEROGENEN SYSTEMEN MIT HILFE VON $Co^{60}$ ALS INDIKATOR*

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**Abstract**—The kinetics of the distribution of radioactivity in suspensions of solid cobalt oxyquinolate and anthranilate in an aqueous and radioactively labelled cobalt-chloride solution were investigated between 100 and 190°C. It was established that the cobalt bound in the solid compounds is not capable of exchange, despite the high temperature.

The processes which bring about a distribution of the activity throughout the system, in spite of this lack of exchangeability, were investigated. From the distribution of activity in the oxyquinolate case the solubility and the heat of solution in an aqueous medium could be determined up to 190°C. In the anthranilate case a chemical change in the solid phase led to an enrichment of the activity in the originally inactive solid phase. The enrichment and the conditions for its occurrence were quantitatively investigated, and it was shown how the velocity of the reaction in the solid phase can be deduced from the measured distribution of activity.

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## 1. EINLEITUNG

BEI der Untersuchung von Austauschreaktionen mit Hilfe von radioaktiven Isotopen an fest-flüssigen Systemen tritt oft der komplizierende Fall ein, dass durch eine Instabilität der festen Phase, sei es Alterung, Umkristallisation oder gar chemische Veränderung, ein Austausch vorgetäuscht wird.

In dieser Arbeit wird an zwei Systemen gezeigt, dass die Arbeitsmethoden der Untersuchung von heterogenen Austauschsystemen auch geeignet sind, typische Fälle von instabilen Systemen quantitativ zu erfassen. Die untersuchten Systeme setzten sich zusammen aus den in der analytischen Chemie verwendeten Verbindungen: Kobaltanthranilat und -oxychinolat als Festkörper und einer wässerigen Kobaltchloridlösung. Die organischen Kobaltverbindungen wurden deshalb gewählt, weil es von Interesse war, in Ergänzung zu den oft untersuchten Ionengittern auch Auskunft über das Austauschverhalten von Molekülgitterstrukturen zu erhalten.

Ausserdem wird gezeigt, da sich eine messbare Verteilung der Aktivität erst über 100°C beobachten liess, dass die Methode der Markierung mit radioaktiven Isotopen mit einfachen experimentellen Mitteln wertvolle Aufschlüsse bei der Untersuchung physikalisch-chemischer Vorgänge in fest-flüssigen Systemen oberhalb des Siedepunktes der flüssigen Phase liefert; in einem Temperaturbereich also, der wegen des herrschenden Ueberdruckes eine direkte chemische Untersuchung sehr erschwert.

### *Allgemeine Bemerkungen zu den Experimenten*

Zur Untersuchung der Zeitabhängigkeit der Reaktionen wurde eine Suspension der festen Phase in mit $Co^{60}$ markierter Kobaltchloridlösung (31,25 mM $CoCl_2$/1;

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0,4 mCurie/l) in einer Ampulle aus Pyrexglas von genügender mechanischer Festigkeit eingeschmolzen und in einem Luftthermostaten bei der gewünschten Temperatur geschüttelt.

Nach dem Abkühlen wurde der Inhalt, dessen Volumen jeweils 8 ccm betrug, filtriert und die $\gamma$-Aktivität des $Co^{60}$ in einem Aliquot des Filtrates gemessen, wobei die Messung in der üblichen Weise korrigiert wurde. (Für den Fall, da sich die Aktivität der Lösung nur wenig änderte, vgl. Abschnitt 2, wurde die Aktivität in einer Lösung bestimmt, die durch Behandeln der festen Phase mit Salzsäure erhalten wurde.) Die nicht zur Aktivitätsmessung verwendete Phase diente zu analytischen Kobaltbestimmungen.

*Bezeichnungen und Definitionen*

| Phase<br>Versuchdauer | Lösung | | feste Phase | |
|---|---|---|---|---|
| | $t = 0$ | $t$ | $t = 0$ | $t$ |
| Masse Kobalt in $\mu$M | $M_{a_0}$ | $M_a$ | $M_{b_0}$ | $M_b$ |
| relative Masse Kobalt | $m_{a_0}$ | $m_a$ | $m_{b_0}$ | $m_b$ |
| Aktivität in ipm | $A_0$ | $A$ | — | $B$ |
| relative Aktivität | $a_0$ | $a$ | — | $b$ |
| spezifische Aktivität | $\sigma_0$ | $\sigma$ | — | — |

wobei definiert ist:

$$m_a = M_a/(M_a + M_b) \text{ bzw}$$
$$m_b = M_b/(M_a + M_b)$$
$$a = A/(A + B) = A/A_0 \text{ bzw.}$$
$$b = B/(A + B) = B/A_0$$
$$\sigma = a/m_a$$

## 2. VERSUCHE MIT KOBALTOXYCHINOLAT

Die Versuche wurden mit der folgenden Zusammensetzung ausgeführt:

Festkörper 91,3 mg Co-oxychinolat $= 250\ \mu M = M_{b_0}$
Lösung 8 ccm Stammlösung $= 250\ \mu M = M_{a_0}$

Für den Fall einer homogenen Aktivitätsverteilung auf das ganze System müsste sich die Aktivität also je zur Hälfte auf beide Phasen verteilen. In Fig. 1 (S. 127) sind die Ergebnisse zusammengestellt, indem die relative Aktivität der festen Phase gegen die Versuchsdauer aufgetragen ist:
Charakteristisch ist, dass die Aktivität der festen Phase sehr rasch auf einen bestimmten, aber geringen, Wert steigt, welcher bei Temperaturen bis 170°C praktisch unabhängig von der Versuchsdauer bleibt, oberhalb dieser Temperatur aber langsam weiter ansteigt.

Est ist naheliegend, dass der weitere Anstieg von $b(t)$ bei 180 und 190°C einem Umsetzungsprozess zugeschrieben werden muss, wie er ähnlich beim im Abschnitt 3 beschriebenen System auftritt. Oberhalb 170°C wurde nämlich eine zunehmende Veränderung der festen Phase beobachtet, indem sich rotbraune Umsetzungsprodukte bildeten. Unterhalb 170°C zeigte die feste Phase dagegen keine Veränderungen und aus analytischen Kontrollbestimmungen ging hervor, dass das Massenverhältnis konstant geblieben war.

Die Umsetzungsreaktion wurde der langen Versuchsdauer wegen nicht weiter untersucht.

Versuche, bei denen die Suspension gerade nach Erreichen der gewünschten Temperatur wieder abgekühlt wurde, zeigten bereits eine Aktivitätsverteilung, welche praktisch dem auf $t = 0$ extrapolierten Wert von $b(t)$ der entsprechenden Temperatur gleichkam.

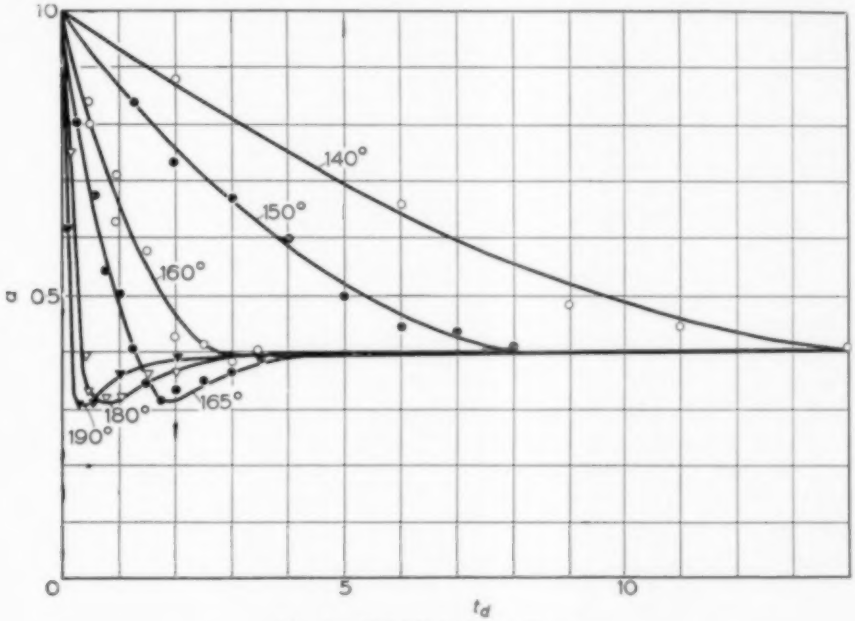


FIG. 1.—Aktivität der festen Phase.

Eine derartige Aktivitätsverteilung kann nicht etwa durch einen beschränkten Austausch zu Stande kommen, denn dann müsste ein vom Nullpunkt ausgehender exponentieller Anstieg zu den konstanten Werten gemessen werden. Es ist also anzunehmen, dass das Kobalt im festen Oxychinolat nicht austauschfähig ist, wobei die mangelnde Austauschfähigkeit eine Eigenschaft der Struktur der festen Verbindung und nicht des Moleküls selbst sein muss. HALL und WILFORD[1] beobachteten nämlich, dass in Pyridin homogen gelöstes Nickeloxychinolat und -chlorid bei Zimmertemperatur in wenigen Minuten vollständig austauschen.

Besitzt aber das Oxychinolat eine bestimmte Löslichkeit und ist das Kobalt im gelösten Oxychinolat austauschfähig, so wird sich beim Erhitzen der Suspension das Löslichkeitsgleichgewicht bei der höheren Temperatur einstellen, worauf sich der gelöste Anteil mit der Lösungsaktivität ins Gleichgewicht setzen wird. Beim Abkühlen wird der gelöste Anteil wieder auskristallisieren und dabei eine zeitunabhängige und konstante Aktivitätsmenge in die feste Phase bringen.

Durch Messung dieser Aktivitätsmenge wird es also ermöglicht die in Lösung gegangene Menge zu berechnen.[2]

[1] N. HALL und B. WILFORD *J. Amer. Chem. Soc.* **73**, 5419 (1951).
[2] P. JORDAN *Mitteilung in Helv. Phys. Acta* **26**, 378 (1953).

Ausgehend vom Verhältnis $M_b/M_a = M_{b_0}/M_{a_0}$ sei $\alpha M_b$ der in Lösung gegangene Bruchteil der festen Phase. Bei der höheren Temperatur verteilt sich sodann die Anfangsaktivität der Lösung $A_0$ auf die Kobaltmasse $M_a + \alpha M_b$. Wenn beim Abkühlen auf die Ausgangstemperatur $\alpha M_b$ wieder auskristallisiert, werden sich die Aktivitäten der beiden Phasen verhalten wie:

$$B : A = \alpha M_b : M_a$$

und

$$\alpha M_b = M_a \frac{B}{A} = M_a \frac{b}{a} = M_a \frac{b}{a_0 - b}$$

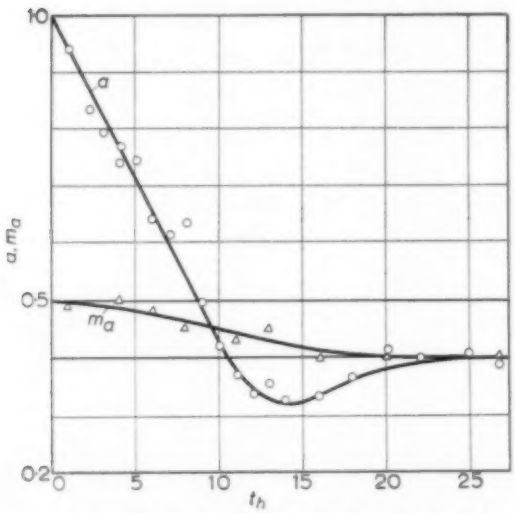


FIG. 2.—$\alpha M_b$ in Funktion des Volumens $V_a$ der Lösung.
——— berechnet für Löslichkeit 2,4 mM/l.

Zur weiteren Bestätigung der Annahme, nach welcher der beobachtete Austausch auf eine begrenzte Auflösung der festen Phase zurückzuführen ist, wurden folgende Versuche bei konstanter Temperatur (170°C) und einer konstanten Versuchsdauer ($2d$) ausgeführt:

1. Zu einem bestimmten Volumen der Stammlösung wurden steigende Mengen Kobaltoxychinolat zugesetzt und festgestellt, dass die Aktivität der festen Phase und damit die daraus berechnete Menge $\alpha M_b$ unabhängig von der Menge Oxychinolat ist.

2. Die gleiche Menge Oxychinolat wurde zu steigenden Volumina der Stammlösung zugesetzt. Dabei geht der Volumenvergrösserung entsprechend mehr feste Phase in Lösung, d.h. $\alpha M_b$ wächst linear mit dem Volumen der Lösung. (Vgl. Fig. 2.)

3. Die gleiche Menge Oxychinolat wurde zu gleichen Volumina von Lösungen gleicher Anfangsaktivität, aber steigender Kobaltkonzentration zugesetzt. In allen Versuchen geht die gleiche Menge Oxychinolat in Lösung, beim Abkühlen wird jedoch durch den gelösten Anteil praktisch die ganze Lösungsaktivität in die feste Phase mitgeführt, falls die Konzentration der Lösung gering ist oder umgekehrt wird für grosse Konzentrationen die Aktivität der festen Phase vernachlässigbar klein werden. (Vgl. Fig. 3.)

Zur Berechnung der Temperaturabhängigkeit der Löslichkeit wurden die auf $t = 0$ extrapolierten Werte von $b(t)$ in Fig. 1 verwendet:

| $t$°C | $10^3 \cdot T^{-1}$ | $b_{extr}$ | Löslichkeit mM/l. |
|---|---|---|---|
| 90 | 2,755 | 0,003 | 0,09 |
| 100 | 2,580 | 0,004 | 0,13 |
| 120 | 2,545 | 0,015 | 0,48 |
| 140 | 2,421 | 0,026 | 0,8 |
| 160 | 2,309 | 0,053 | 1,8 |
| 170 | 2,257 | 0,067 | 2,4 |
| 180 | 2,207 | 0,092 | 3,2 |
| 190 | 2,159 | 0,126 | 4,5 |

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Durch Auftragen der berechneten Werte für die Löslichkeit im halblogarithmischen Masstab gegen $1/T$ zeigt sich ein linearer Zusammenhang, vgl. Fig. 4, so dass für den untersuchten Temperaturbereich die Berechnung der Lösungswärme $L$ nach Clausius-Clapeyron möglich ist:

$$d \ln C/dt = L/RT^2$$

und

$$L = 13 \text{ kcal/Grad.Mol.}$$

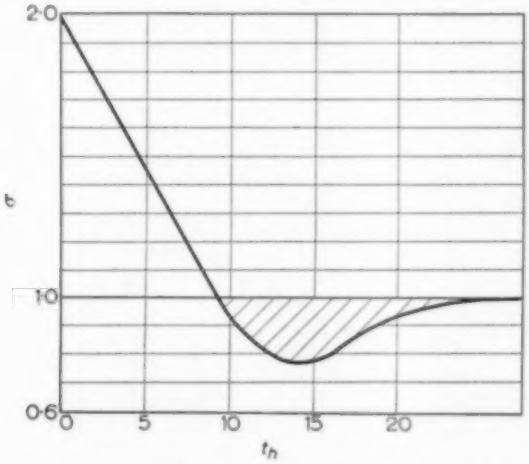


FIG. 3.—$b$ in Funktion der Konzentration $C$ der Lösung.
——— berechnet für Löslichkeit 2,4 mM/l.

## 3. VERSUCHE MIT KOBALTANTHRANILAT

Analog zum vorhergehenden System war die Zusammensetzung:

Festkörper 82,8 mg Co-anthranilat = 250 $\mu$M Co = $M_{b_0}$
Lösung 8 ccm Stammlösung = 250 $\mu$M Co = $M_{a_0}$

und die Ergebnisse im untersuchten Temperaturbereich sind in Fig 5 zusammengestellt, indem die relative Aktivität der Lösung gegen die Versuchsdauer aufgetragen ist.

Charakteristisch sind folgende Erscheinungen:

1. Unter 130°C wird der Gleichgewichtswert erst nach sehr langer Zeit erreicht.

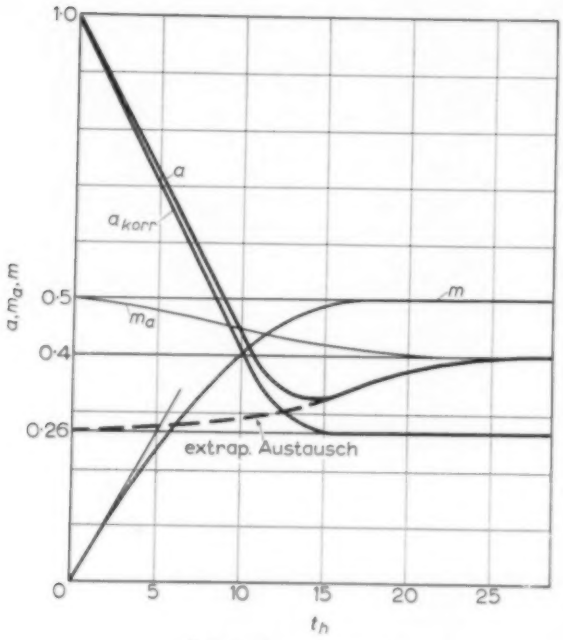


FIG. 4.—Lösungswärme

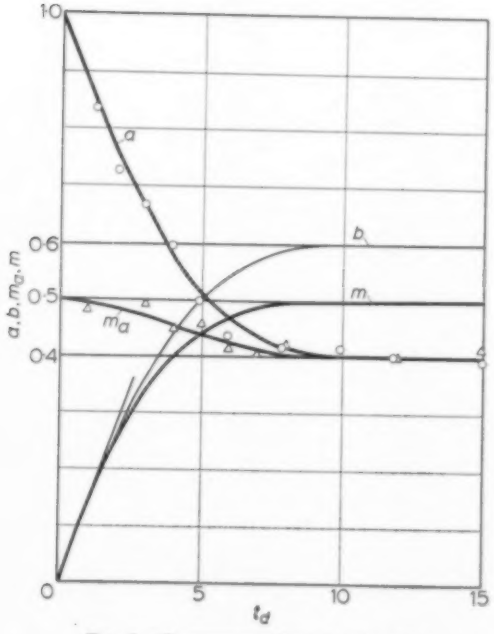


FIG. 5.—Zusammenstellung der Resultate.

2. Unter 160°C fällt $a(t)$ stetig gegen einen Gleichgewichtswert, welcher tiefer liegt, als der aus dem Anfangsverhältnis der Massen geforderte. (Die Aktivität sollte sich wiederum je zur Hälfte auf beide Phasen verteilen.)
3. Oberhalb 160°C erreicht $a(t)$ den Gleichgewichtswert erst nach dem Durchlaufen eines Minimums.
4. Der Gleichgewichtswert ist innerhalb des Versuchsfehlers der gleiche für alle untersuchten Temperaturen.

Die erste Erscheinung lässt sich rasch erklären, wenn die Aktivitätsverteilung mit dem analytisch bestimmten Kobaltgehalt der Lösung verglichen wird. Als Beispiel

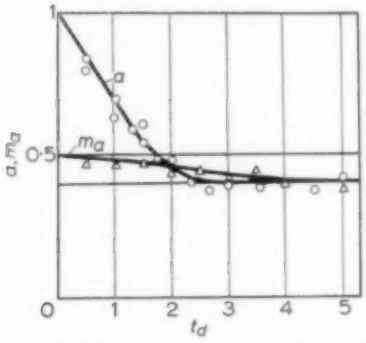


FIG. 6.—Aktivität und Kobaltgehalt der Lösung in Funktion der Zeit bei 180°C.

dienen die Versuche bei 180°C, vgl. Fig. 6. Es zeigt sich, dass sich im Laufe des Versuchs das Massenverhältnis $m_{a_0}/m_{b_0}$ verschoben hat, indem ein Teil des Kobalts der Lösung in die feste Phase übergegangen ist, (durch welchen Prozess, soll später behandelt werden) und damit ändert sich natürlich auch das Aktivitätsgleichgewicht. (Da $m_a$ und $a$ als Relativwerte am gleichen Ordinatenmasstab gemessen wurden, ist das einfach ersichtlich, indem sowohl $m_a(t)$ als auch $a(t)$ gegen den gleichen Grenzwert streben.)

In Fig. 6 zeigt sich aber gleichzeitig, dass die Veränderung von $m_a/m_b$ die Minimumsbildung in $a(t)$ nicht erklärt, da im Bereich des Minimums kein direkter Zusammenhang zwischen $a(t)$ und $m_a(t)$ besteht. Diese Tatsache wird verdeutlicht, wenn an Stelle von $a$ die spezifische Aktivität der Lösung, $\sigma = a/m_a$, gegen die Versuchsdauer aufgetragen wird, vgl. Fig. 7.

Es zeigt sich, dass im schraffierten Bereich $\sigma < 1$ ist, was nichts anderes bedeutet, (da aus der Definition von $\sigma$ hervorgeht, dass für $t = 0$ $\sigma_0 = a_0/m_a = 2$ und für homogene Aktivitätsverteilung $\sigma = a_0/(m_a + m_b) = 1$ ist,) dass die Lösung an Aktivität verarmt ist, bzw. dass sich die Aktivität in der ursprünglich inaktiven festen Phase angereichert hat. Der weitere Verlauf von $\sigma(t)$ zeigt, dass diese Verarmung, bzw. Anreicherung nur vorübergehend ist, da nach dem Durchlaufen des Minimums $\sigma$ gegen 1 ansteigt, d.h. das System erreicht schliesslich doch die homogene Aktivitätsverteilung.

Dieses Verhalten des Systems entspricht also nicht demjenigen eines reinen heterogenen Austauschsystems. Aber schon die Veränderung des Massenverhältnisses $m_a/m_b$ deutet darauf hin, dass die Erklärung in einer chemischen Umwandlung des Systems zu suchen ist.

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In der Tat wurde festgestellt, dass unter den Versuchsbedingungen das System instabil ist, und dass das Kobaltanthranilat nach Erreichen des Aktivitätsgleichgewichtes völlig in eine neue feste Kobaltverbindung umgewandelt ist.

Die chemische und röntgenographische Untersuchung dieser Verbindung ergab ein basisches Kobaltsilikat, dessen Zusammensetzung (45% Co, 37% $SiO_2$, 18% $H_2O$ = mittlere Zusammensetzung der im Gleichgewicht befindlichen festen Phase im untersuchten Temperaturbereich) und Debye-Scherrer-auf nahme vergleichbar war mit einem Präparat, welches von FEITKNECHT durch längeres Erhitzen von einer wässerigen

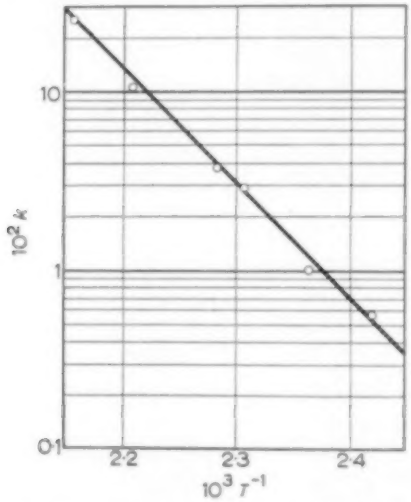


FIG. 7.—Spezifische Aktivität der Lösung in Funktion der Zeit bei 180°C.

Suspension von grünem basischen Kobaltbromid auf 200°C im Einschmelzrohr erhalten wurde.[3] Daneben wurden $CO_2$, Anilin, dagegen keine freie Anthranilsäure festgestellt.

Es wäre denkbar, dass sich das Kobaltanthranilat direkt auf der Glasoberfläche zu einem basischen Kobaltsilikat umwandelt. Dieser Vorgang würde aber keineswegs zu einer Änderung des Aktivitätsverhältnisses führen. Es muss also vielmehr die Lösung eine entscheidende Rolle spielen: in erster Linie muss in Betracht gezogen werden, dass gelöstes Kobaltchlorid bei höheren Temperaturen eine zunehmende Tendenz zeigt zu basischen Verbindungen zu hydrolisieren, z.B. nach folgender Gleichung:

$$CoCl_2 + 2H_2O = Co(OH)_2 + 2HCl \qquad (1)$$

Durch Hydrolyse bildet sich unlösliches Kobalthydroxyd und freie Salzsäure. Wird letztere nicht neutralisiert, verhindert sie natürlich das Ausfallen von Hydroxyd. Tatsächlich wurde festgestellt, dass eine reine Kobaltchloridlösung, unter den gleichen Versuchsbedingungen erhitzt, völlig unverändert blieb.

Befindet sich dagegen im System noch Kobaltanthranilat suspendiert, so kann folgende Reaktion stattfinden:

$$Co(anthr)_2 + 2HCl = CoCl_2 + 2H(anthr)_2 \qquad (2)$$

[3] W. FEITKNECHT und A. BURGER *Helv. Chim. Acta* **25**, 1541 (1942).

Durch die Bindung der Salzsäure kann nun nach (1) gelöstes Kobalt ausfallen. Gleichzeitig geht aber eine entsprechende Menge Kobalt aus dem festen Kobaltanthranilat in Lösung, welches wiederum nach (1) weiterreagiert, usw., bis der gesamte Vorgang schliesslich mit dem völligen Verbrauch des Kobaltanthranilates zum Stillstand kommt. (Ein chemisches Gleichgewicht wird nicht erreicht, da wie bereits oben angedeutet, die gebildete freie Anthranilsäure durch Decarboxylierung in $CO_2$ und Anilin aus dem System entfernt wird. Zur Decarboxylierung von Anthranilsäure vgl.[4].

Die Bildung von Anilin verursacht ihrerseits durch die alkalische Reaktion eine pH-verschiebung im System, wodurch teils die Ausfällung einer zusätzlichen Menge Kobalt aus der Lösung, teils der Angriff des Reaktionsgemisches auf die Glaswand erklärt wird. Erstere führt zur beobachteten Verschiebung des Massenverhältnisses, letzterer zur Bildung des basischen Kobaltsilikates aus primär gebildetem Hydroxyd.

Der endgültige Effekt dieses Reaktionsmechanismus ist damit: das gelöste Kobalt des Systems fällt in Form einer neuen festen Verbindung aus, während die ursprüngliche feste Phase im gleichen Masstabe aufgelöst wird.

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Sind nun die Kobaltatome der Lösung markiert, so ist leicht einzusehen, dass durch die chemische Umsetzung aktive Atome nur aus der Lösung in die feste Phase gelangen können und nie umgekehrt. Der Transport markierter Teilchen in die ursprünglich inaktive Phase ist dadurch viel kräftiger, als bei einem gewöhnlichen Austauschsystem, bei welchem umso mehr markierte Atome wieder aus der ursprünglich inaktiven Phase fortwandern, je weiter der Prozess gediehen ist.

Endlich muss noch berücksichtigt werden, dass sich solche gewöhnliche Austausch-prozesse zwischen den Bestandteilen der festen Phase, d.h. Kobaltanthranilat und basischem Kobaltsilikat, und der Lösung abspielen können. Für den Fall des Kobaltanthranilates ist eine Austauschfähigkeit, wie im Fall des Kobaltoxychinolates, aus strukturellen Gründen nicht zu erwarten. (Da ein solcher Austausch der Anreicherung der Aktivität durch die chemische Umsetzung entgegenwirken würde, kann aus den Experimenten heraus diese Annahme als vernünftig betrachtet werden.) Dagegen erklärt sich der vorübergehende Charakter der Aktivitätsanreicherung, wenn eine Austauschfähigkeit der neugebildeten basischen Verbindung angenommen wird. Folgendes Experiment bestätigt diese Annahme: Unter den gleichen Versuchsbedingungen wie bei den aktiven Versuchen wurde ein inaktiver Versuch bei 160, bzw. 190°C 4 bzw. 2 Tage erhitzt, um das System in das Umsetzungsgleichgewicht zu versetzen. Anschliessend wurde die Ampulle geöffnet, der Lösung aktives Kobalt zugesetzt und darauf wieder zugeschmolzen. Damit konnte bei den entsprechenden Temperaturen der Austausch zwischen dem basischen Kobaltsilikat und der Lösung nach Ablauf der Umsetzungsreaktion und der Verschiebung des Massenverhältnisses gemessen werden. Wie erwartet, tauscht das System vollständig aus mit einer Halbwertszeit von 10 bzw. 3,5, h, und als Grenzwert tritt natürlich der durch das neue Massenverhältnis bestimmte Wert auf.

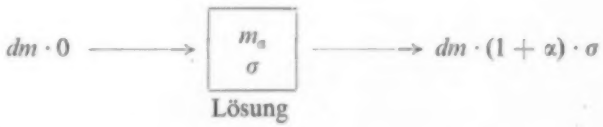
Für die Aktivitätsverteilung im System Kobaltanthranilat—Kobaltchloridlösung kommen damit zwei voneinander unabhängige Prozesse in Betracht: einerseits der Aktivitätstransport aus der Lösung in die feste Phase durch die chemische Umsetzung und andererseits der Austausch der Aktivität zwischen der neugebildeten festen Phase und der Lösung.

[4] N. Stevens *et al. Canad. J. Chem.* **30**, 529 (1952).

Das Aussehen der Funktion $a(t)$ hängt damit vom Geschwindigkeitsverhältnis der beiden Teilprozesse ab. Eine Anreicherung der Aktivität wird nur möglich sein, wenn die Austauschreaktion die in die feste Phase gelangende Aktivität nicht genügend rasch abbauen kann, wie es bei den Temperaturen über 160°C der Fall ist. Unter 160°C überwiegt die Austauschreaktion und verhindert dadurch die Aktivitätsanreicherung. (Vgl. auch KOLTHOFF,[5, 6] der bei Umkristallisationsvorgängen eine Anreicherung der Aktivität beobachtete, die aber einer quantitativen Auswertung nicht ohne weiteres zugänglich ist.)

Eine interessante Frage ist nun, wie gross der Anreicherungseffekt maximal werden kann, d.h. wenn angenommen wird, dass die entstehende Verbindung nicht austauschfähig ist, wenn also die ganze aus der Lösung fortgeführte Aktivität unverändert in der festen Phase gespeichert wird. Im nun folgenden mathematischen Ansatz soll also nur der Aktivitätstransport durch die Umsetzungsreaktion und durch zusätzliche Ausfällung von gelöstem Kobalt eingehen.

Mit den eingangs angeführten Bezeichnungen lässt sich folgende Aktivitätsbilanz in einem beliebigen Zeitpunkt t aufstellen: Zur Zeit t befindet sich in der Lösung die Kobaltmasse $m_a$, wobei $m_a = m_{a_0} - \alpha m$ ist, d.h. die Kobaltmasse $m_{a_0}$ hat sich um den Betrag $\alpha m$, ausgedrückt als Bruchteil der zur Zeit t bereits durch die Lösung hindurchgewanderten Kobaltmasse $m$ ausgedrückt, verringert.



Lösung

In die Lösung ($m_a$, $\sigma$) soll ein Massenelement $dm$ aus der inaktiven festen Phase eintreten und unter Berücksichtigung der zusätzlichen Ausfällung die Masse $dm + \alpha dm$ austreten. Es wird dabei angenommen, dass die in die Lösung eintretenden Kobaltatome sich sofort homogen mit denen der Lösung vermischen, d.h. die austretende Kobaltmasse hat in jedem Zeitpunkt die gleiche spezifische Aktivität wie die Lösung. Die Kobaltmasse $dm + \alpha dm$ wird also die Aktivitätsmenge $(1 + \alpha) \cdot dm \cdot \sigma$ mitführen. Diese muss aber gleich dem Unterschied der Aktivität der Lösung vor Eintritt von $dm$, nämlich $m_a \cdot \sigma$, und derjenigen nach Austritt von $(1 + \alpha) \cdot dm$, nämlich $(m_a - \alpha dm) \cdot (\sigma + d\sigma)$, sein:

$$(1 + \alpha) \cdot dm = m_a \cdot \sigma - (m_a - \alpha dm) \cdot (\sigma + d\sigma)$$

Durch Vereinfachen erhält man folgende Differentialgleichung:

$$-\sigma \cdot dm = (m_{a_0} - \alpha m) \cdot d\sigma$$

Durch Separieren und Integrieren mit den Anfangsbedingungen $m = 0$ und $\sigma = \sigma_0$ erhält man die spezifische Aktivität der Lösung in Funktion der durch die Lösung hindurchgewanderten Menge $m$:

$$\sigma = \sigma_2 \cdot \left(1 - \frac{\alpha m}{m_{a_0}}\right)^{1/\alpha} \tag{3}$$

[5] J. KOLTHOFF und C. ROSENBLUM *J. Amer. Chem. Soc.* **58**, 116 (1936).
[6] J. KOLTHOFF und F. EGGERTSEN *J. Amer. Chem. Soc.* **63**, 1412 (1941).

und die entsprechende relative Aktivität durch Einsetzen von $\sigma = a/(m_{a_0} - \alpha m)$ und $\sigma_0 = a_0/m_{a_0}$:

$$a = a_0 \cdot \left(1 - \frac{\alpha m}{m_{a_0}}\right)^{1/\alpha} \tag{4}$$

Für $0 < m/m_{a_0} < 1$ wurde $\alpha$ experimentell als 0,2 bestimmt und damit die folgenden Werte für a gemäss der obigen Formel berechnet. Als Vergleich ist ausserdem die Aktivität für den Fall homogener Aktivitätsverteilung beim Verhältnis $m/m_a$ berechnet:

TABELLE 1

| $m/m_{a_0}$ | $m$ | $a$ für homog. Verteilung | $a$ ber. nach Gleichung (4) |
|---|---|---|---|
| 0,093 | 0,05 | 0,95 | 0,941 |
| 0,111 | 0,10 | 0,90 | 0,871 |
| 0,177 | 0,15 | 0,85 | 0,806 |
| 0,250 | 0,20 | 0,80 | 0,737 |
| 0,333 | 0,25 | 0,75 | 0,661 |
| 0,420 | 0,30 | 0,70 | 0,584 |
| 0,538 | 0,35 | 0,65 | 0,510 |
| 0,667 | 0,40 | 0,60 | 0,424 |
| 0,819 | 0,45 | 0,55 | 0,342 |
| 1,000 | 0,50 | 0,50 | 0,262 |

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Für das angewandte Verhältnis $m_{b_0}/m_{a_0} = 1$ würde also die Aktivität der Lösung auf 0,262 gegenüber 0,5 bei homogener Verteilung sinken. Wenn experimentell dieser Wert nicht erreicht wird, das Minimum von $a(t)$ liegt bei 0,32, vgl. Fig. 5, so ist das eben der Effekt des Austausches der entstehenden festen Phase mit der Lösung, der im Ansatz unberücksichtigt geblieben ist. (Eine Berücksichtigung dieses Austausches im Ansatz wäre schwierig, denn es liegt hier ein sehr komplexes System vor, da zuerst das Austauschsystem aufgebaut werden muss, was zur Folge hat, dass das Massenverhältnis der Partner nicht konstant ist und dass aufeinanderfolgend gebildete neue feste Phase mit verschiedener spezifischer Aktivität ausfällt.)

Mit der obigen Berechnung und den experimentellen Kurven gelingt es aber, diesen Austauscheffekt graphisch zu berücksichtigen, wie am Beispiel der Kurve für 180°C gezeigt wird (vgl. Fig. 8). Als interessante Anwendung kann dabei die Umsetzungsgeschwindigkeit des Anthranilates bestimmt werden.

Die experimentell bestimmte Kurve $a(t)$ erreicht den Grenzwert 0,263 nicht, da der Austausch als Gegenspieler auftritt. Der Effekt dieses Austauschs lässt sich aber leicht extrapolieren, vgl. die Kurve "extrapolierter Austausch." Die Ordinatenabschnitte zwischen dieser Kurve und dem Grenzwert 0,263 sind gerade gleich den Aktivitätsmengen, welche durch Austausch in die Lösung zurückgebracht wurden. Zu Beginn des Versuches ist diese Aktivität gleich Null, anschliessend steigt sie entsprechend dem Auftreten der neuen festen Phase, und nach dem Minimum in $a(t)$ läuft natürlich der extrapolierte Austausch in die experimentelle Kurve $a(t)$ aus.

Subtrahiert man in jedem Zeitpunkt diese Abschnitte von den entsprechenden Werten $a(t)$, so erhält man die Kurve $a(t)_{korr}$, d.h. den Aktivitätsverlauf in Funktion der ZEIT ohne Berücksichtigung des Austausches. Andererseits gibt die oben abgeleitete Formel (4) den Aktivitätsverlauf in Funktion der umgesetzten MASSE, ebenfalls ohne Berücksichtigung des Austausches.

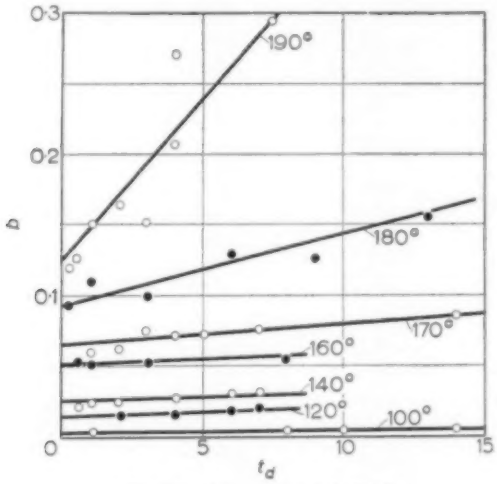


FIG. 8.—Auswertung bei 180°C.

Durch Gleichsetzen der entsprechenden Aktivitätswerte $a(t)$ und $a(m)$ erhält man für jede Versuchszeit die bereits durch die Lösung hindurchgewanderte Kobaltmasse, d.h. die umgesetzte Masse Anthranilat in Funktion der Zeit.

(Praktisch erhält man diese Kurve $m(t)$ indem man die in Tabelle 1 aus Gleichung (4) berechneten Werte $a(m)$ auf der Kurve $a(t)_{korr}$ aufsucht und auf deren Ordinate den Tabellenwert für $m$ aufträgt.)

Unter 160°C vereinfacht sich die Bestimmung der umgesetzten Masse Anthranilat wesentlich, denn jetzt überwiegt die Austauschgeschwindigkeit und man kann in diesem Fall annehmen, dass die neugebildete feste Phase ständig im Austauschgleichgewicht mit der Lösung steht, d.h. die Aktivität der Lösung verhält sich zu derjenigen der festen Phase, wie die Masse Kobalt in Lösung zu derjenigen, die dem neugebildeten Teil der festen Phase angehört.

In Fig. 9 stellt $b(t) = 1 - a(t)$ also den Aktivitätsverlauf in der festen Phase dar. Durch die Darstellung in relativen Werten ist $b(t)$ numerisch gleich der Masse des neugebildeten Teiles der festen Phase. Dieser Teil ist aber zusammengesetzt aus direkt aus der Lösung ausgefallenem Kobalt und durch Umsetzung des Anthranilat ausgefallenem Kobalt.

Erstere Menge wurde aber analytisch bestimmt, sie wird durch die Ordinatenabschnitte $0{,}5 - m_a$ gemessen und durch Subtraktion dieser Abschnitte von $b(t) = m_b(t)$ erhält man die gesuchte Kurve $m(t)$.

Ergänzend ist noch festzustellen, dass bei 160°C gerade das Uebergangsgebiet liegt, in welchem sich die Umsetzungs- und die Austauschgeschwindigkeit die Wage halten.

Fig. 10 zeigt, dass die Teilprozesse zufällig so zusammenwirken, dass in $a(t)$ kein Minimum zur Ausbildung kommt. Aus der Tatsache aber, dass sich $a(t)$ und $m_a(t)$ überschneiden (da beide wieder als Relativwerte gemessen werden) ist abzuleiten, dass im Bereich von 2 bis 5 Tagen eine Aktivitätsanreicherung in der festen Phase eintritt. Eine Auswertung nach einer der beschriebenen zwei Methoden ist also hier nicht statthaft.

Zur Charakterisierung des Umsetzungsvorganges wurde die Neigung der Ursprungstangente an die eben graphisch ermittelten Kurven $m(t)$ bestimmt, da diese die Geschwindigkeitskonstante $k$ zur Zeit $t = 0$ angibt, in einem Moment also, in welchem die Umsetzungsreaktion noch unbeeinflusst von den Reaktionsprodukten abläuft.

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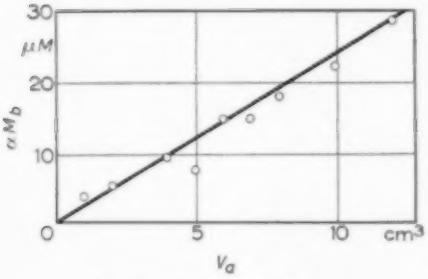


FIG. 9.—Auswertung bei 150°C.

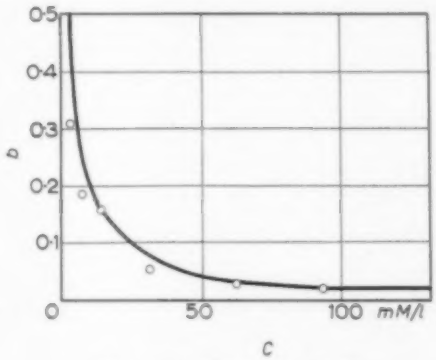


FIG. 10.—Auswertung bei 160°C.

Die Werte sind in Tabelle 2 zusammengestellt, wobei $k$ als pro Stunde umgesetzter Bruchteil des Kobaltanthranilates ausgedrückt ist:

TABELLE 2.

| $t$°C | $k$ |
|---|---|
| 140 | 0,0058 |
| 150 | 0.0103 |
| 165 | 0,035 |
| 180 | 0,105 |
| 190 | 0,256 |

Durch Auftragen dieser $k$-Werte im logarithmischen Masstab gegen $1/T$ erhält man eine Gerade (vgl. Fig. 11), deren Steigung gemäss dem Arrhenius'schen Ansatz:

$$\ln k = -E_{akt}/RT + \text{const}$$

die Aktivierungsenergie $E_{akt}$ des Vorganges misst. Diese wurde aus Fig. 11 mit $E_{akt} =$ 29 kcal/Grad.Mol bestimmt.

Vergegenwärtigt man sich nochmals die Vorstellungen von dem Chemismus des gesamten Vorganges, so muss festgehalten werden, dass diese Aktivierungsenergie

nur als eine Angabe der Grössenordnung gewertet werden darf und ohne weitere chemische Untersuchungen über den Rahmen dieser Arbeit hinaus, besonders ohne Berücksichtigung der Temperaturabhängigkeit der chemischen Aktivität der an der

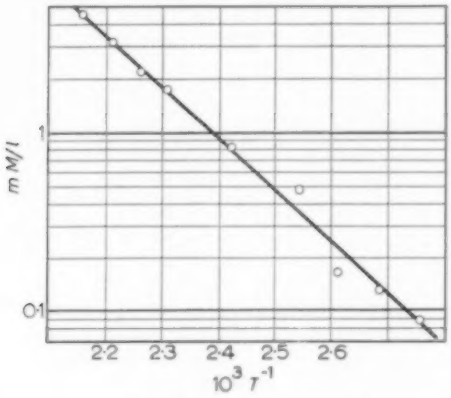


FIG. 11.—Aktivierungsenergie

Reaktion beteiligten gelösten Stoffe, nicht etwa einer bestimmten Teilreaktion zugeschrieben werden darf. Trotz dieser Einschränkung ist aber die Konstanz der Aktivierungsenergie bemerkenswert, was immerhin auf einen einheitlichen Reaktionsmechanismus für den untersuchten Temperaturbereich schliessen lässt.

Für die ständige Unterstützung und das grosse Interesse an dieser Arbeit sei Herrn Prof. Dr. P. SCHERRER herzlich gedankt.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 139 to 152. Pergamon Press Ltd., London

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# ÜBER TANTALSÄURE UND DIE WASSERLÖSLICHEN ALKALITANTALATE

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**Abstract**—In an extensive study, the degree of condensation of polytantalic acid has been investigated. By application of physicochemical and analytical methods it is shown, that to ascribe to alkaline tantalates a formulation as hexatantalate $4Me_2^IO{\cdot}3Ta_2O_5{\cdot}16H_2O$ is unjustified. The alkaline tantalates prepared and analysed by us according to a modified method of analysis possess a ratio $Me_2^IO : Ta_2O_5 = 1{\cdot}40 : 1{\cdot}00$, i. e. 7 : 5, corresponding to the formula $Me_7Ta_5O_{16}{\cdot}aq$. By optical measurements with solutions of alkaline tantalates it was confirmed that there are no alterations of constitution within the whole alkaline region. The molecular weight of the anion of potassium tantalate determined by measurements of the coefficient of diffusion agrees well with the calculated value according to the supposed formula. From measurements of the depression of freezing-point in saturated solutions of potassium nitrate it is evident that the tantalate anion contains five atoms of tantalum, while conductivity measurements demonstrate the existence of a heptabasic polytantalic acid.

Thus the investigated salts are to be considered as alkaline pentatantalates $7Me_2^IO{\cdot}5Ta_2O_5{\cdot}aq.$, which are derived from pentatantalic acid $H_7(Ta_5O_{16})$. The latter may easily be formulated as an orthotantalic acid $H_3TaO_4$, whose four O-atoms are substituted by $(TaO_4)$-groups. According to our investigations, no evidence as to the existence of hexa- or deca-tantalic acid could be found.

DIE ersten umfangreichen Arbeiten über Tantalsäuren und Alkalitantalate stammen von H. ROSE.[1] Er beschreibt eine Vielzahl dieser Salze und findet für das Verhältnis Basenoxyd : Säureoxyd, $Me_2^IO : Ta_2O_5$, Werte, die zwischen 5 : 1 und 1 : 3 schwanken.

Später beschäftigte sich C. MARIGNAC[2] mit dem gleichen Thema und unterzog das von ROSE gegebene Material einer kritischen Sichtung. Er kam dabei zu der Feststellung, daß ROSES Präparate stets mehr oder weniger Niob enthalten haben. Die Untersuchungen MARIGNACS gipfeln in der Behauptung, daß eindeutige Verbindungen nur sie sogenannten Metatantalate, $Me_2^IO : Ta_2O_5 = 1 : 1$, und die Hexatantalate, $Me_2^IO : Ta_2O_5 = 1{,}33 : 1$, darstellten, wobei letztere aus einer Kondensation von drei Molekülen der Metasäure hervorgegangen seien. Die Metatantalate sollen beim starken Erhitzen der Hexatantalate entstehen und unlöslich in Wasser sein. Außerordentlich bemerkenswert ist die Tatsache, daß die von MARIGNAC mitgeteilten Analysen von Kalium- und Natriumtantalaten, die er zum Beweis der von ihm vermuteten Hexatantalatform anführt, durchweg mehr Alkali enthalten als einem Hexatantalat entsprechen würde.

Im Rahmen des Arbeitsgebietes "Amphotere Oxydhydrate" untersuchten G. JANDER und H. SCHULZ[3, 3a] Alkalitantalate und fanden ohne Ausnahme ein mittleres

[1] H. ROSE *Pogg. Annalen.* **100,** 551; **101,** 11; **102,** 55 (1857).
[2] C. MARIGNAC *Ann. Chim. phys.* **49,** 249 (1866); *Liebigs Annalen, Suppl. bd.* **4,** Heft 3, S. 350 (1866).
[3] G. JANDER und H. SCHULZ *Z. anorg. Chem.* **144,** 225 (1925).
[3a] H. SCHULZ Dissertation Göttingen 1924.

Molverhältnis $Me_2^IO : Ta_2O_5 = 1{,}40 : 1$ bzw. 7 : 5, aus dem die Existenz einer Pentatantalsäure folgt. Sie konnten dieses Ergebnis noch erhärten durch die Bestimmung des spezifischen Diffusionskoeffizienten des Tantalatanions in wässriger Lösung, der erstmalig gestattete, das Molekulargewicht dieses aggregierten Anions annähernd zu berechnen.

F. WINDMAISSER,[4] der ebenfalls Kaliumtantalat untersuchte, kommt zu dem überraschenden Ergebnis, daß sowohl das Pentatantalat als auch das Hexatantalat existieren muß. Infolge eines noch ungeklärten Einflusses wechselte die Zusammensetzung der von ihm erhaltenen Tantalate zwischen den Formeln $7K_2O{\cdot}5Ta_2O_5{\cdot}24H_2O$ und $4K_2O{\cdot}3Ta_2O_5{\cdot}16H_2O$. Chemische Unterschiede zwischen beiden Salztypen waren nicht feststellbar; auch die Kristallstruktur war identisch, wie aus einer röntgenographischen Untersuchung[5] beider Salze hervorgeht. WINDMAISSER betrachtete sie daher als eine Verbindung mit einer durch Austauschbarkeit von HOH gegen KOH veränderlichen Zusammensetzung innerhalb obiger Grenzformeln.

Eine kürzlich erschienene Arbeit von I. LINDQUIST und B. ARONSSON[6] befaßt sich mit der röntgenographischen Untersuchung von Kaliumhexatantalat. Die Verfasser führten eine komplette Strukturanalyse durch und finden, daß das Salz $4K_2O{\cdot}3Ta_2O_5{\cdot}16H_2O$ als $K_8Ta_6O_{19}{\cdot}16H_2O$ zu formulieren sei. Sie bezweifeln die Existenz eines Pentatantalates auf Grund der von G. JANDER und H. SCHULZ durchgeführten Diffusionsversuche, deren Ergebnisse nach ihrer Ansicht eher auf die Existenz eines Hexatantalates hinweisen, geben jedoch gleichzeitig zu bedenken, daß erst eine eingehende Untersuchung durchzuführen sei, ehe endgültig behauptet werden kann, ob das Hexatantalation $[Ta_6O_{19}]^{8-}$ auch in wässriger Lösung existiert.

*Darstellung und Beschreibung der Alkalitantalate*

Als Ausgangsmaterial für die folgenden Untersuchungen stand uns Tantalpentoxyd hoher Reinheit zur Verfügung.

Zur Darstellung der Alkalitantalate beschritten wir den bereits von H. ROSE[1] und G. MARIGNAC[2] gewiesenen Weg des KOH-bzw. $K_2CO_3$-Aufschlusses des Tantalpentoxyds, der zunächst zum Kaliumsalz führt. Wegen seiner relativ guten Wasserlöslichkeit kann man daraus durch doppelte Umsetzungen viele andere Tantalate erhalten, von denen das Lithium- und Natriumsalz schwerer löslich, die Schwermetalltantalate sämtlich unlöslich in Wasser sind. Die Salze wurden von der Mutterlauge abgesaugt, kurz mit kaltem Wasser, Äthanol und Aceton gewaschen und im Exsiccator über CaO aufbewahrt.

(1) *Kaliumtantalat.* ROSE[1] und MARIGNAC[2] haben 1 Gewichtsteil $Ta_2O_5$ mit 2 bis 3 Gewichtsteilen KOH im Silbertiegel klar geschmolzen; das entspricht etwa einem Molverhältnis $Ta_2O_5$ : KOH = 1 : 25. Auch wir hielten uns prinzipiell an diese Vorschrift. Zum Lösen des zerkleinerten Schmelzkuchens wurde entweder heißes oder eiskaltes Wasser verwendet. Im letzten Fall achteten wir besonders darauf, daß beim Lösevorgang ein positiver Wärmeeffekt nach Möglichkeit vermieden wurde. Es zeigte sich nämlich, daß man auf diese Weise zwei verschiedene Hydrate des Kaliumtantalates erhalten kann. Die Lösungen ließen wir bis zur völligen Klärung stehen, dekantierten dann vom Silberschlamm ab, filtrierten und überließen sie schließlich bei Zimmertemperatur im Exsiccator über CaO der Kristallisation. Die Dauer des Kristallisationsvorganges ist maßgebend für Größe und Art der entstehenden Kaliumtantalatkristalle.

[4] F. WINDMAISSER *Z. anorg. Chem.* **248**, 283 (1941).
[5] F. WINDMAISSER, F. HALLA, und A. NETH *Z. Kristallographie* (*A*) **104**, 161 (1941).
[6] I. LINDQUIST und B. ARONSSON *Arkiv. för Kemi* **7**, 49 (1954).

Läßt man der Kristallisation reichlich Zeit, so entstehen im allgemeinen gut ausgebildete, mitunter bis zu 1 cm große Kristalle, die mit dem in der Literatur beschriebenen Kaliumtantalat identisch sind; wir bezeichneten es als Kaliumtantalat I (*Abb.* 1).

Hat man dagegen den Schmelzkuchen in relativ wenig heißem Wasser gelöst, und läßt man die Kristallisation im Vakuumexsikkator über konzentrierter $H_2SO_4$ verhältnismäßig schnell vonstatten gehen, dann entstehen in der Regel mikroskopisch kleine Kristalle, deren Kristallwassergehalt gegenüber Kaliumtantalat I geringer ist. In der Literatur ist es noch nicht erwähnt; wir bezeichneten es als Kaliumtantalat II.

In einem Falle gelang es uns, ein drittes Kaliumsalz zu erhalten, dessen Kristallform sich von den beiden anderen wesentlich unterscheidet. Es handelt sich um flache, sechseckige Scheiben von etwa 5 mm Durchmesser. Alle Versuche, diese Kristalle nochmals darzustellen, scheiterten jedoch. Auch dieses Kaliumsalz ist in der Literatur bisher noch nicht beschrieben worden; wir bezeichneten es als Kaliumtantalat III.

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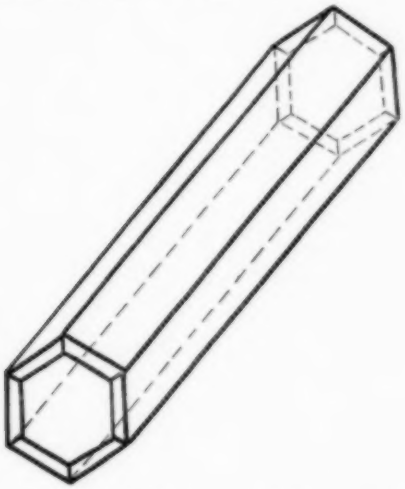

Abb. 1.—Kaliumtantalat I (schematisch).

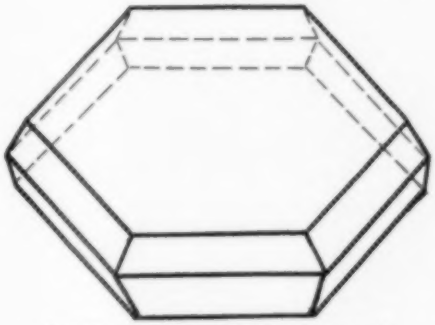

Abb. 2.—Natriumtantalat I (schematisch).

(2) *Natrium- und Lithiumtantalat*. Wir fällten Natriumtantalat durch Zugabe von Natronlauge zu Kaliumtantalatlösungen aus. Auch hier kann man zwei verschiedene Hydrate erhalten, die sich in ihrer Kristallform scharf voneinander unterscheiden.

Die eine Form war schon H. Rose[1] und C. Marignac[2] bekannt. Man erhält sie, wenn eiskalte Kaliumtantalatlösungen mit kalter Natronlauge versetzt werden. Das Natriumsalz scheidet sich in mikroskopisch kleinen kompakten Kristallen ab; wir bezeichneten es als Natriumtantalat I (*Abb.* 2).

Das andere Hydrat wurde erstmalig von G. Jander und H. Schulz[3] beobachtet und rein dargestellt, indem sie heiße Kaliumtantalatlösungen mit heißer Natronlauge versetzten. Der kristalline Niederschlag, der sich häufig erst nach geraumer Zeit bildet, besteht aus mikroskopisch kleinen, verästelten Kristallnadeln. Entsprechend seiner Darstellungsweise ist dieses Natriumtantalat ärmer an Kristallwasser, auch seine Löslichkeit bleibt etwas hinter der der Sechsecke zurück; wir bezeichneten es als Natriumtantalat II.

Versetzt man Kaliumtantalatlösungen mit konzentrierter Lithiumhydroxdlösung, so erhält man nach einiger Zeit einen weißen, kristallinen Niederschlag, der aus mikroskopisch kleinen Oktaedern mit abgeflachten Ecken besteht.

(3) *Rubidium- und Caesiumtantalat*. Ein inniges Gemisch von 2 Gewichtsteilen Rubidium- bzw. Caesiumkarbonat mit 1 Gewichtsteil $Ta_2O_5$ (Molverhältnis etwa 4 : 1 bzw. 3 : 1) erhitzten wir im Platintiegel bis zum klaren Schmelzfluß. Der Schmelzkuchen wurde in wenig Wasser gelöst und die Lösung im Vakuumexsikkator über konzentrierter Schwefelsäure zur Kristallisation gebracht. Nach einigen Tagen entstanden in beiden Fällen große, sechseckige Kristalle bis zu 2 cm Durchmesser. Beide Tantalate lösen sich sehr leicht in Wasser.

*Analysenmethode und -ergebnisse*

Die Analysen von Alkalitantalaten wurden bisher in der Weise ausgeführt, daß Tantalpentoxydhydrat aus den wässrigen Lösungen durch Zugabe verdünnter Mineralsäuren, durch $SO_2$ oder $CO_2$ gefällt und nach dem Abfiltrieren zu $Ta_2O_5$ verglüht und ausgewogen wurde. Die Alkalibestimmung erfolgte durch Eindampfen des Filtrats und Überführen in das Sulfat. Gelegentlich versuchte man, den Kristallwassergehalt der Tantalate aus dem Glühverlust zu berechnen. Die Salze zersetzten sich jedoch beim Glühen, wobei freies Alkalihydroxyd abgespalten wird, das sehr leicht Feuchtigkeit und $CO_2$ aus der Luft aufnimmt. Die so erhaltenen Werte sind daher mit Skepsis zu betrachten; schon C. MARIGNAC[2] verwirft aus diesem Grunde eine direkte Wasserbestimmung.

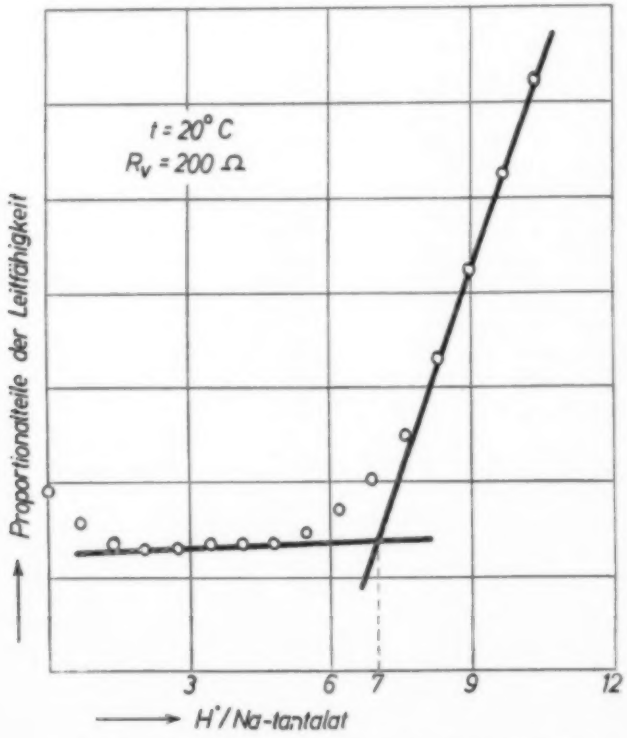


ABB. 3.—Konduktometrische Titration von Natriumtantalat ($1{,}503 \cdot 10^{-4}$ Mol) mit $0{,}104n$ $H_2SO_4$.

Wir wandelten diese bisher übliche Analysenmethode etwas ab. Verwendet man nämlich zur Fällung von Tantalpentoxydhydrat statt $SO_2$ eine genau bekannte Menge $n$/10-$H_2SO_4$ im Überschuß, dann kann man den Alkaligehalt des Salzes, nach Rücktitration der unverbrauchten Säure mit $n$/10-NaOH, aus dem Säureverbrauch berechnen. Voraussetzung für dieses Verfahren ist die Annahme daß die Dissoziationskonstanten der freien Tantalsäure außerordentlich klein sind, so daß durch die Schwefelsäure lediglich das (durch Hydrolyse abgespaltene) Alkalihydroxyd erfaßt wird. Um einen Einblick in den Neutralisationsverlauf zu erhalten, führten wir eine konduktometrische Titration einer Alkalitantalatlösung mit $n$/10-$H_2SO_4$ durch, deren Ergebnis aus *Abb.* 3 ersichtlich ist.

Die sinngemäße Extrapolation der Kurvenäste ergibt, daß der Äquivalenzpunkt erreicht ist, wenn 7 Wasserstoffionen auf 1 Tantalsäurerest entfallen. Es läge danach also eine siebenbasische Polytantalsäure vor, und man kann die der Titration zugrunde liegende Reaktionsgleichung wie folgt formulieren:

$$2Na_7[Ta\ldots]_x{\cdot}aqu. + 7H_2SO_4 \rightarrow 2H_7[Ta\ldots]_x{\cdot}aqu. + 7Na_2SO_4$$

$$2H_7[Ta\ldots]_x{\cdot}aqu. \rightarrow 7H_2O + \frac{x}{2}\,Ta_2O_5{\cdot}aqu.$$

Wir untersuchten anschließend den Niederschlag von Tantalpentoxydhydrat nach gründlichem Auswaschen spektralanalytisch auf einen Gehalt von Alkali, wobei wir fanden, daß bei den Lithium-, Natrium- und Kaliumsalzen das Ergebnis stets negativ, dagegen bei den Rubidium- und Caesiumsalzen positiv ausfiel. Offenbar werden also die größeren, und damit wenig hydratisierten Alkaliionen bevorzugt vom Tantalpentoxydhydratniederschlag adsorbiert. Das hat zur Folge, daß die Analysenergebnisse von Rubidium- und Caesiumtantalat sämtlich etwas hinter den zu erwartenden Werten zurückbleiben; ein Gesichtspunkt, der selbstverständlich auch bei gravimetrischen Alkalibestimmungen zu beachten ist.

Das Filtrat des Tantalpentoxydhydratniederschlages enthielt neben überschüssiger Schwefelsäure nur Alkalisulfat. Den Kristallwassergehalt der untersuchten Salze ermittelten wir stets durch Ergänzung der gefundenen Prozentzahlen für $Ta_2O_5$ und $Me_2^IO$ zu 100.

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Die von uns untersuchten Alkalitantalate und die erhaltenen Analysenergebnisse, sowie die daraus abgeleiteten Bruttoformeln sind in Tabelle 1 zusammengestellt.

Von einer Anzahl der analysierten Natriumtantalate I und II wurden zur Prüfung auf einheitliche Zusammensetzung der Salze Debye-Scherrer-Aufnahmen hergestellt. Aus deren Identität geht hervor, daß jeweils einheitliche Substanzen vorliegen, sodaß die geringfügigen Schwankungen der berechneten Molverhältnisse innerhalb eines Salztyps auf Analysenfehler zurückzuführen sind.

Die Tatsache, daß sämtliche untersuchten Alkalitantalate ausnahmslos ein mittleres Molverhältnis $Me_2^IO : Ta_2O_5 = 1{,}40 : 1$ bzw. $7 : 5$ aufweisen, widerlegt die Marignacsche Auffassung von der Existenz eines Hexatantalats, dem ein Molverhältnis $Me_2^IO : Ta_2O_5 = 1{,}33 : 1$ bzw. $4 : 3$ entsprechen würde, und gibt gleichzeitig gegenüber den Arbeiten von F. WINDMAISSER,[4, 5] nach denen sowohl das Pentatantalat als auch das Hexatantalat, als Grenzfälle eines Homogenitätsbereiches, existieren soll, zu großen Bedenken Anlaß.

Auf Grund unserer Analysen leiten sich die Alkalitantalate vielmehr ausschließlich von der Pentatantalsäure ab, als deren höchstbasische Salze sie zu betrachten sind. Lediglich der Kristallwassergehalt der Salze scheint innerhalb gewisser Grenzen zu schwanken; aus diesem Grunde legen wir auch keinen Wert auf eine definitive Angabe bezüglich der Anzahl von Kristallwassermolekeln.

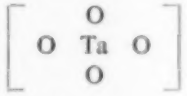
Die beim Rubidium- und Caesiumtantalat gefundenen Werte für das Verhältnis $Me_2^IO : Ta_2O_5 = 1{,}37 : 1$ bzw. $1{,}36 : 1$, die vom Mittelwert $1{,}40 : 1$ abweichen, erklären sich aus der Feststellung, daß Rubidium- und Caesiumionen vom Tantalpentoxydhydratniederschlag bevorzugt adsorbiert werden und damit der Alkalibestimmung entgehen. Daß jedoch auch bei diesen Salzen Pentatantalate vorliegen, geht aus den Absorptionsspektren hervor, die mit denen der übrigen Alkalitantalate übereinstimmen.

Das Molverhältnis $Me_2^IO : Ta_2O_5 = 1{,}40 : 1$ bzw. $7 : 5$ erscheint im ersten Augenblick kompliziert. Die resultierende Bruttoformel $Me_{14}^ITa_{10}O_{32}{\cdot}aqu.$ ist jedoch durch zwei teilbar und ergibt dann $Me_7^ITa_5O_{16}{\cdot}aqu.$ Danach kann man sich die

Tabelle 1.

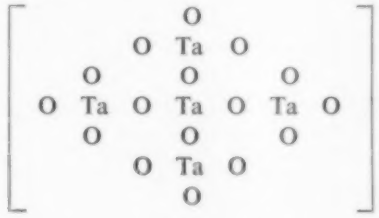
| | $\%Ta_2O_5$ | $\%Me_2^IO$ | $\%H_2O$ | Molverhältnis |
|---|---|---|---|---|
| *Kaliumtantalat I* | | | | $7K_2O{\cdot}5Ta_2O_5{\cdot}24H_2O$ |
| Mittelwerte aus | 66,85 | 19,98 | 13,17 | 1 : 1,40 : 4,87 |
| 7 Analysen: | ±0,26 | ±0,31 | | ±0,02 |
| Mittlere Abweichung: | | | | |
| Berechnet für | | | | |
| obige Formel: | 66,92 | 19,98 | 13,10 | 1 : 1,40 : 4,80 |
| *Kaliumtantalat II* | | | | $7K_2O{\cdot}5Ta_2O_5{\cdot}15H_2O$ |
| Mittelwerte aus | | | | |
| 6 Analysen: | 70,35 | 20,93 | 8,72 | 1 : 1,40 : 3,05 |
| Mittlere Abweichung: | ±0,45 | ±0,17 | | ±0,01 |
| Berechnet | | | | |
| obige Formel: | 70,38 | 21,01 | 8,61 | 1 : 1,40 : 3,00 |
| *Kaliumtantalat III* | | | | $7K_2O{\cdot}5Ta_2O_5{\cdot}20(21)H_2O$ |
| Mittelwerte aus | | | | |
| 2 Analysen: | 68,29 | 20,26 | 11,45 | 1 : 1,40 : 4,12 |
| Mittlere Abweichung | ±0,01 | ±0,10 | | ±0,01 |
| Berechnet für | | | | |
| obige Formel: | 68,42 | 20,42 | 11,16 | 1 : 1,40 : 4,00($20H_2O$) |
| | 68,04 | 20,31 | 11,65 | 1 : 1,40 : 4,20($21H_2O$) |
| *Natriumtantalat I* | | | | $7Na_2O{\cdot}5Ta_2O_5{\cdot}37H_2O$ |
| 1 Analyse: | 66,89 | 13,07 | 20,04 | 1 : 1,39 : 7,35 |
| Berechnet für | | | | |
| obige Formel: | 66,75 | 13,11 | 20,14 | 1 : 1,40 : 7,40 |
| *Natriumtantalat II* | | | | $7Na_2O{\cdot}5Ta_2O_5{\cdot}22H_2O$ |
| Mittelwerte aus | | | | |
| 7 Analysen: | 72,72 | 14,28 | 13,00 | 1 : 1,40 : 4,39 |
| Mittlere Abweichung: | ±0,72 | ±0,22 | | ±0,01 |
| Berechnet für | | | | |
| obige Formel: | 72,68 | 14,28 | 13,04 | 1 : 1,40 : 4,40 |
| *Lithiumtantalat* | | | | $7Li_2O{\cdot}5Ta_2O_5{\cdot}47H_2O$ |
| Mittelwerte aus | | | | |
| 2 Analysen: | 67,67 | 6,37 | 25,96 | 1 : 1,40 : 9,40 |
| Mittlere Abweichung: | ±0,10 | ±0,02 | | ±0,01 |
| Berechnet für | | | | |
| obige Formel: | 67,66 | 6,40 | 25,94 | 1 : 1,40 : 9,40 |
| *Rubidiumtantalat* | | | | $7Rb_2O{\cdot}5Ta_2O_5{\cdot}22H_2O$ |
| Mittelwerte aus | | | | |
| 3 Analysen: | 56,98 | 32,95 | 10,07 | 1 : 1,37 : 4,34 |
| Mittlere Abweichung: | ±0,54 | ±0,29 | | ±0,01 |
| Berechnet für | | | | |
| obige Formel: | 56,44 | 33,44 | 10,12 | 1 : 1,40 : 4,40 |
| *Caesiumtantalat* | | | | $7Cs_2O{\cdot}5Ta_2O_5{\cdot}18H_2O$ |
| 1 Analyse: | 49,58 | 42,92 | 7,50 | 1 : 1,36 : 3,71 |
| Berechnet für | | | | |
| obige Formel: | 48,83 | 43,61 | 7,56 | 1 : 1,40 : 3,60 |

Alkalitantalate von einer Isopolysäure abgeleitet denken, bei der die Sauerstoffatome der Orthotantalsäure $H_3TaO_4$



$[TaO_4]^{3-}$

durch den Säurerest $(TaO_4)^{3-}$ ersetzt sind:



$[Ta_5O_{16}]^{7-}$

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Es ist nun außerordentlich wichtig und aufschlußreich, durch direkte Molekulargewichtsbestimmungen einen Anhaltspunkt für die Molekulargröße des Tantalatanions in Alkalitantalatlösungen zu erhalten. Besonders interessant ist die Beantwortung der Frage, ob eine Penta- oder etwa eine Dekatantalsäure vorliegt und ob sich vielleicht aus Messungen der Diffusionsgeschwindigkeit und der Lichtabsorption in Abhängigkeit vom pH-Wert der Lösungen ein Existenzgebeit der umstrittenen Hexatantalsäure ergeben würde.

*Lichtabsorptionsmessungen an Alkalitantalatlösungen*

Finden in den Alkalisalzlösungen schwacher anorganischer Basen oder Sauerstoffsäuren Kondensationsvorgänge statt, so machen sich diese Änderungen der Konstitution durch charakteristische Verschiebungen der Absorptionsspektren bemerkbar. Je höhermolekular die in der Lösung beständigen Hydrolyseprodukte sind, desto flacher und ausgeglichener wird der Verlauf der Absorptionskurve. Gleichzeitig verschiebt sich der Beginn der Lichtabsorption mit steigendem Aggregationsgrad nach größeren Wellenlängen hin.[7a] Die Messung der Lichtabsorption gestattet daher schnell und sicher, Aggregationsvorgänge zu erkennen.

Die praktische Durchführung unserer Absorptionsmessungen erfolgte nach dem von G. SCHEIBE[7] beschriebenen Verfahren. Zur Änderung der Wasserstoffionenkonzentration in den einzelnen Lösungen verwendeten wir stets KOH bzw. $HClO_4$, die beide in dem in Betracht kommenden Spektralgebiet optisch "leer" sind. Um Fehler durch geringe Trübungen zu vermeiden, die Absorptionserscheinungen vortäuschen könnten, wurden alle Lösungen prinzipiell durch Membranfilter (Durchlässigkeitsstufe "feinst") filtriert. Sämtliche Absorptionskurven wurden auf den Gehalt an $Ta_2O_5$ der Lösungen bezogen.

Wir fanden, daß alle untersuchten Lösungen das gleiche Absorptionsspektrum (*Abb.* 4) lieferten. Daraus ergibt sich, daß im alkalischen Gebiet nur Teilchen eines ganz bestimmten Aggregationsgrades vorhanden sind und daß keinerlei Konstitutionsänderungen stattfinden, gleichgültig ob die Hydroxylionenkonzentration sehr groß oder nur relativ gering ist.

[7] G. SCHEIBE *Ber.* **57**, 1330 (1924).
[7a] G. JANDER und TH. ADEN *Z. physikal. Chem.* (*A*) **144**, 197 (1929).

*Bestimmung der Molekulargröße des Tantalatanions durch Messung der Diffusionsgeschwindigkeit*

Die üblichen Methoden der Molekulargewichtsbestimmung sind auf das vorliegende Problem der Untersuchung hydrolysierender Systeme im allgemeinen nicht anwendbar, da die stets vorhandenen Begleitelektrolyte, wie freie Säure oder Base, nicht genau genug bestimmt und in Rechnung gesetzt werden können. Dagegen hat sich die Messung des Diffusionsvermögens der Teilchen zur Bestimmung der angenäherten Molekulargröße ausgezeichnet bewährt, da die Diffusionsgeschwindigkeit eines gelösten Stoffes hauptsächlich von der Teilchengröße abhängig ist.

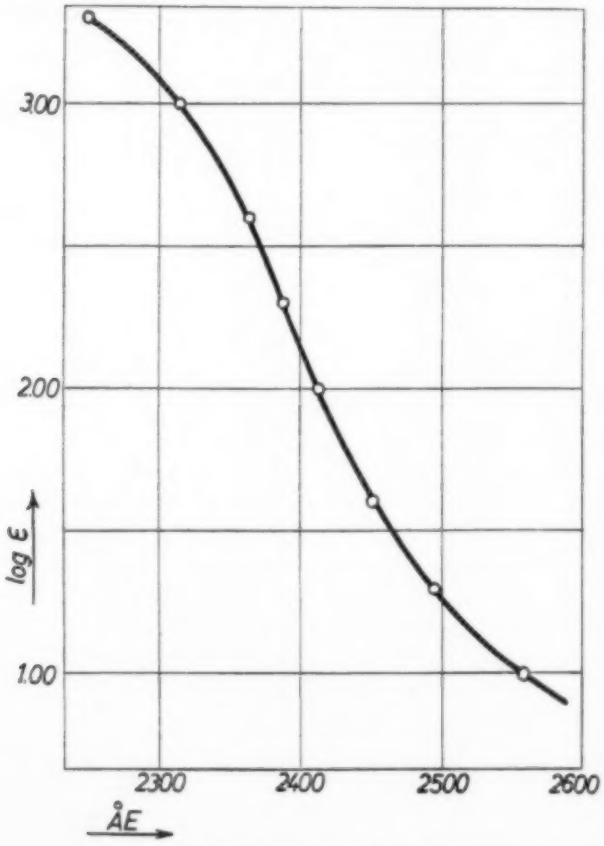


ABB. 4.—Absorptionsspektrum d. Alkalitantalate

Zur Durchführung unserer Diffusionsmessungen bedienten wir uns der Methode von OEHOLM,[8] deren Anwendbarkeit zur Untersuchung der Vorgänge in hydrolysierenden Systemen, insbesondere hinsichtlich der Iso- und Heteropolyverbindungen, von I. BERTRAM[9] und G. JANDER und H. SCHULZ[10] eingehend geprüft und experimentell durchgearbeitet wurde. Wir ersetzten bei der dort beschriebenen Apparatur Stopfen und Quetschhähne durch Glasschliffe und eingeschliffene Hähne. Die zu untersuchende wässrige Lösung war von der Bodenschicht von Hg durch eine 1 bis 2 cm hohe Schicht von Tetrachlorkohlenstoff getrennt (siehe *Abb. 5*).

[8] L. W. OEHOLM *Z. physikal. Chem.* **50,** 309 (1905); **70,** 378 (1910).
[9] I. BERTRAM Diplomarbeit Greifswald 1952.
[10] G. JANDER u. H. SCHULZ *Kolloid-Z., Ergbd.* **36,** 109 (1925).

Bezüglich Einzelheiten der Methode und Auswertung der Versuchsergebnisse verweisen wir auf entsprechende Literaturstellen. [9-13]

Mit Rücksicht auf den Gültigkeitsbereich des Fickschen Gesetzes führten wir unsere Diffusionsversuche an verdünnten Kaliumtantalatlösungen durch, die 0,1 äquivalentnormal an Kaliumtantalat waren. Durch Einstellen auf bestimmte pH-Werte tasteten wir das alkalische Gebiet systematisch ab. Nach dem Herstellen der Versuchslösungen überließen wir dieselben noch einige Tage sich selbst und warteten eine eventuelle Gleichgewichtseinstellung ab; dann wurden sie der Diffusion unterworfen.

Die Ergebnisse unserer Versuche sind aus *Abb.* 6 zu ersehen, in der die gefundenen Diffusionskoeffizienten in Abhängigkeit von der Hydroxylionenkonzentration graphisch dargestellt sind. Aus der Konstanz der spezifischen Diffusionskoeffizienten geht hervor, daß im alkalischen Gebiet keinerlei Aggregationsvorgänge stattfinden. In den Lösungen existieren daher nur Teilchen bestimmter Größe; ein Ergebnis, das unsere Lichtabsorptionsmessungen vollauf bestätigen.

Wir hofften, im stark alkalischen Gebiet (3*m*-KOH) eine Aufspaltung des Polytantalatanions zu erreichen, stellten jedoch fest, daß auch hier die gleiche Teilchengröße wie in den weniger stark alkalischen Bereichen vorliegen muß. Ein Abbau der vorilegenden Polytantalsäure, z.B. bis zur Orthotantalsäure $H_3TaO_4$, ist also offensichtlich in wässriger Lösung unmöglich.

Wir erhielten aus unseren Diffusionsversuchen einen mittleren spezifischen Diffusionskoeffizienten $\overline{D_{10} \cdot z} = 0{,}26$. Damit bestätigen unsere Messungen im wesentlichen die Ergebnisse von G. JANDER und H. SCHULZ.[3]

Um eine Berechnung der Molekulargröße des Tantalatanions durchführen zu können, untersuchten wir hinsichtlich ihres Diffusionsvermögens eine Verbindung mit einem gemäß der oben gegebenen Formulierung der Tantalate ähnlich großem Molekulargewicht und einem womöglich ähnlichen Aufbauprinzip. Dazu schien uns das Natriumhexamolybdänsäureperjodat $Na_5[J(MoO_4)_6]\cdot 17H_2O$ gut geeignet, dessen Anionengewicht 1087 beträgt, während dem Pentatantalatanion ein solches von 1160 entsprechen würde. Die Darstellung des Natriumhexamolybdänsäureperjodats erfolgte nach einer von BLOMSTRAND[13] gegebenen Vorschrift. Für die Diffusionsversuche kamen wieder 0,1 äquivalentnormale Lösungen dieses Salzes zur Anwendung, denen wir durch Zusatz von $HNO_3$ bestimmte pH-Werte erteilten. Auch hier bewahrten wir die Lösungen erst einige Tage auf, um eine

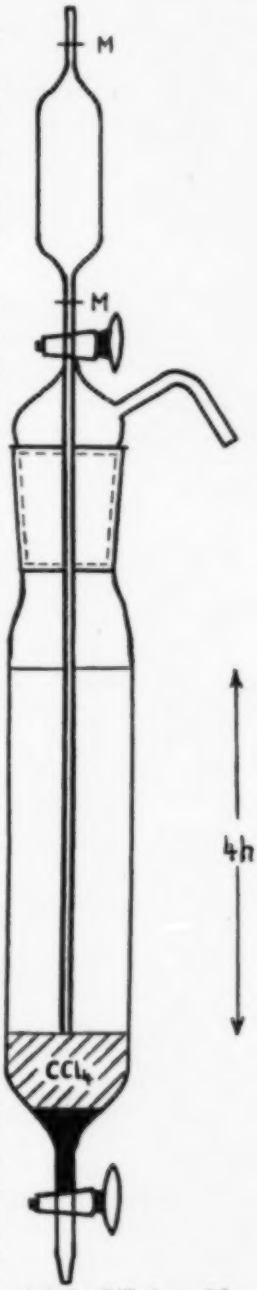

ABB. 5.—Diffusionsgefäß.

[11] J. STEFAN *Ber. kaiserl. Akad. Wien, Math.-nat. Klasse* **79**, Abt. II, 167 (1879).
[12] W. KAWALKI *Wied. Ann.; neue Folge* **52**, 166 u. 300 (1894).
[13] BLOMSTRAND *Z. anorg. Chem.* **1**, 10 (1892).

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Gleichgewichtseinstellung abzuwarten. Aus der graphischen Darstellung unserer Versuchsergebnisse (*Abb.* 7) ergibt sich ebenfalls eine Konstanz der Diffusionskoeffizienten, als deren Mittelwert wir $\overline{D_{10} \cdot z} = 0{,}27$ errechneten.

Eine gewisse chemische Analogie und der vielleicht nicht unähnliche Aufbau der

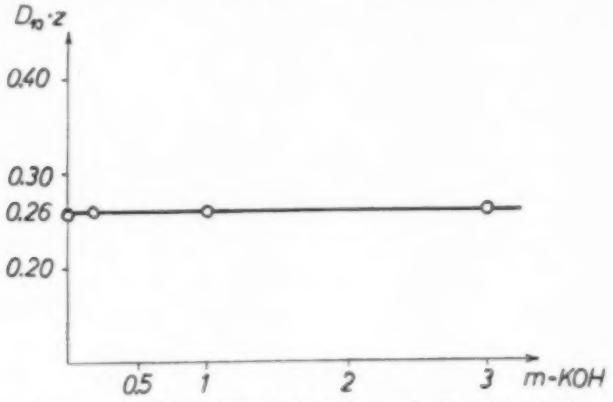


ABB. 6.—Spezifische Diffusionskoeffizienten des Tantalatanions in KOH-Lösungen verschiedener Molarität.

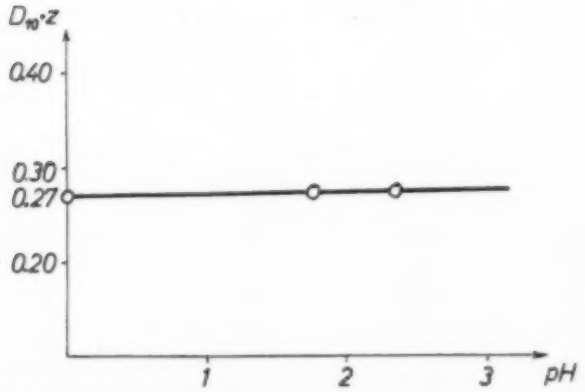


ABB. 7.—Spezifische Diffusionskoeffizienten des Anions $[J(MoO_4)_6]^{5-}$ in salpetersauren $NaNO_3$-Lösungen.

beiden untersuchten Salze gestattet die Anwendung der eingeschränkten Rieckeschen Beziehung:[14, 15, 16,)]

$$\overline{(D_{10} \cdot z)_1} \cdot \sqrt{M_1} = \overline{(D_{10} \cdot z)_2} \cdot \sqrt{M_2}$$

zur Berechnung des angenäherten Anionengewichtes der Tantalate.

Setzt man die gefundenen Werte 0,26 für das Tantalatanion und 0,27 für das Hexamolybdänsäureperjodatanion in obige Gleichung ein, so erhält man

$$\sqrt{M_{\text{Tantalat}}} = \frac{0{,}27}{0{,}26} \cdot \sqrt{1087}$$

[14] G. JANDER u. A. WINKEL *Z. anorg. Chem.* **193**, 1 (1930).
[15] RIECKE *Z. physikal. Chem.* **6**, 564 (1890).
[16] G. JANDER u. A. WINKEL *Z. physikal. Chem.* (*A*) **149**, 97 (1930).

und daraus

$$M_{\text{Tantalat}} = 1172.$$

Aus der zur Diskussion stehenden Formulierung des Kaliumtantalates, wie sie sich aus dem einfachsten Verhältnis der Analysenresultate ergibt, berechnet sich das Anionengewicht des Kaliumtantalates zu

$$(Ta_5O_{16})^{7-} = 1160.$$

Da der aus den Analysen abgeleitete Wert für das Anionengewicht praktisch mit dem aus unseren Diffusionsversuchen berechneten übereinstimmt, ergibt sich somit eindeutig die Existenz einer Pentatantalsäure im gesamten alkalischen Bereich. Bemerkenswert ist die Tatsache, daß die Existenz der Hexatantalsäure, die als höheraggregiertes Produkt erfahrungsgemäß im schwächer alkalischen Gebiet beständig sein sollte, sowohl aus unseren Diffusionsversuchen, wie auch aus unseren Lichtabsorptionsmessungen nicht ersichtlich ist!

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*Salzkryoskopische Messungen am System Kaliumtantalat—Eis—Kaliumnitrat*

Kryoskopische Messungen in konzentrierten Salzlösungen haben gegenüber solchen in reinem Wasser zwei fundamentale Vorteile:

(1) Zur Depression des Gefrierpunktes tragen nur solche Ionen bei, die im Lösungsmittelsalz nicht enthalten sind.

(2) Die gemessenen molaren Depressionen $K$ ändern sich im allgemeinen linear mit der Konzentration $c$, während bei reinem Wasser als Lösungsmittel stark gegen die Ordinate ansteigende Kurven erhalten werden, deren Extrapolation auf den Wert $K_0$ für $c = 0$ Schwierigkeiten macht.

Zur Bestimmung unbekannter Ionengewichte ergibt sich daraus die Regel, die kryoskopischen Messungen mit Hilfe eines Lösungsmittelsalzes durchzuführen, in dem das mit dem interessierenden Teilchen verbundene Gegenion bereits enthalten ist.

Bezeichnet man die in das 2. Raoultsche Gesetz

$$\Delta t = K \cdot c$$

eingehende Konzentration des zu untersuchenden Salzes in Molen pro 1000 g Lösungsmittel mit $c$, die Konzentration in Grammatomen des komplexbildenden Elementes (z.B. Ta) in 1000 g Lösungsmittel mit $C$, ferner den Kondensationsgrad, d.h. die Anzahl der Atome des komplexbildenden Elementes im Anion des zu untersuchenden Salzes mit $p$, dann gilt

$$c = \frac{C}{p}$$

und damit

$$\Delta t = K \cdot \frac{C}{p} \qquad \text{bzw.} \qquad p = \frac{K \cdot C}{\Delta t}.$$

In Lösungssystemen, in denen der Kondensationsgrad $p$ von vornherein nicht bekannt ist, läßt sich auch $c$ vorerst nicht angeben. $C$ ist aber immer bekannt, sodaß auf diesem Wege $p$ bestimmt werden kann.

In einem Diagramm zeichnet man den Wert $K/p$ als Funktion von $C$ und bestimmt den Grenzwert der molaren Gefrierpunktserniedrigung für unendliche Verdünnung $K_0/p$ durch eine lineare Extrapolation. Mit dem aus einer weiteren Messung bestimmten Wert $K_0$ berechnet man dann den Kondensationsgrad.

Die folgenden Messungen wurden nach der von K. F. Jahr und Mitarbeitern[17] ausgearbeiteten und erprobten Methode durchgeführt. Zur Festlegung der molaren Depression im System Eis-$KNO_3$ nahmen wir zunächst salzkryoskopische Messungen

[17] K. F. Jahr, A. Brechlin, M. Blanke und R. Kubens *Z. anorg. Chem.* **270**, 240 (1952).

am System Kaliumchlorid-Eis-Kaliumnitrat vor. Da lösungsmitteleigene Ionen zur Depression nicht beitragen, liegt hier nur ein kryoskopisch wirksames Teilchen ($Cl^-$) vor. Die Versuchslösungen enthielten neben je etwa 4 g $KNO_3$ wachsende Mengen einer 1 m-KCl-Lösung; die Lösungsmittelmenge betrug in allen Fällen insgesamt 25,0 g Wasser. In Tabelle 2 sind unsere Meßergebnisse zusammengestellt; der extrapolierte Wert $K_0 = 1{,}685$ diente uns im folgenden zur Berechnung des Kondensationsgrades des Tantalatanions.

TABELLE 2. Salzkryoskopische Messungen am System KCl-Eis-$KNO_3$

| $c$ (cm³ 1 m-KCl) | $\Delta t$ | $K$ | $K_0$ (extrapoliert) |
|---|---|---|---|
| 0 | 0 | — | 1,685 |
| 5 | 0,359 | 1,795 | |
| 10 | 0,763 | 1,908 | |
| 15 | 1,212 | 2,020 | |

Wir verwendeten für unsere Versuche zur Bestimmung der Molekulargröße des Tantalatanions ausschließlich Kaliumtantalat, das durch seine verhältnismäßig gute Löslichkeit allein in Frage kam. Die zu erwartenden Depressionen sind relativ gering. Jedoch führt die hydrolytische Spaltung von Kaliumtantalat zwangsläufig zu einer Vermehrung der kryoskopisch wirksamen Teilchen. Durch Bestimmung der Hydroxylionenkonzentration in den einzelnen Lösungen und Subtraktion der daraus berechneten zusätzlichen Depressionen von der gemessenen Gefrierpunktserniedrigung ist es indessen möglich, diesen Einfluß weitgehend zu eliminieren. Die Versuchslösungen enthielten neben etwa 4 g $KNO_3$ steigende Mengen Kaliumtantalat. Da die Tantalate durchweg viel Kristallwasser enthalten, wurde der vorher analytisch bestimmte Wassergehalt bei der Einwaage derart berücksichtigt, daß die Gesamtwassermenge der Versuchslösungen genau 25,0 g Wasser betrug. Wir erreichten dadurch, alle Messungen unter gleichen Versuchsbedingungen vornehmen zu können.

Unsere in *Abb.* 8 graphisch dargestellten Versuchsergebnisse erlauben wegen ihrer linearen Abhängigkeit von der Konzentration $C$ eine Extrapolation auf $C = 0$. Die nur bei den höchsten Konzentrationen der Tantalatlösungen auftretenden Abweichungen von der Linearität sind auf Überschreitung der Löslichkeit von Kaliumtantalat zurückzuführen.

Für unendliche Verdünnung ergibt sich ein Wert $K_0/p = 0{,}34_5$, der unter Heranziehung des vorher experimentell festgelegten Wertes $K_0 = 1{,}685$ (siehe Tabelle 2) die Berechnung des Kondensationsgrades $p$ gestattet:

$$p = \frac{1{,}685}{0{,}34_5} = 4{,}88 \simeq 5$$

Im Tantalatanion sind demnach 5 Tantalatome enthalten.

*Zusammenfassung*

(1) Es wird gezeigt, daß die Marignacsche Formulierung der Alkalitantalate als Hexatantalate ungerechtfertigt ist. Aus den von ROSE und MARIGNAC mitgeteilten

Analysen geht hervor, daß die von ihnen untersuchten Alkalitantalate durchweg reicher an Alkali sind als einem Hexatantalat entsprechen würde.

(2) Es werden verschiedene Alkalitantalate dargestellt und beschrieben. Die nach einer modifizierten Analysenmethode von uns erhaltenen Ergebnisse entsprechen bei sämtlichen untersuchten Salzen ohne Ausnahme einem Molverhältnis $Me_2^IO$: $Ta_2O_5 = 1{,}40 : 1{,}00$ bzw. $7 : 5$; lediglich der Kristallwassergehalt schwankt innerhalb gewisser Grenzen. Demgemäß wird den Alkalitantalaten die Bruttoformel $Me_7^ITa_5O_{16}$ · aqu. zugeschrieben.

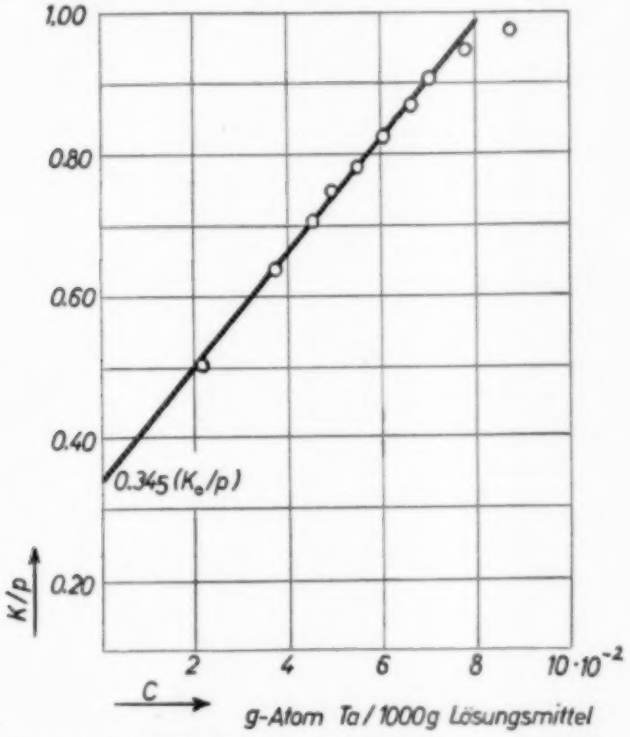


Abb. 8.—Salzkryoskopische Messungen am System Kaliumtantalat-Eis-Kaliumnitrat.

(3) Lichtabsorptionsmessungen an Alkalitantalatlösungen ergeben, daß im gesamten alkalischen Gebiet keine Konstitutionsänderungen stattfinden; vielmehr liegen nur Teilchen eines einzigen, ganz bestimmten Aggregationsgrades vor.

(4) Durch Messung der Diffusionsgeschwindigkeit gelingt eine zahlenmäßige Bestimmung des Anionengewichtes von Kaliumtantalat, das mit dem aus der vermuteten Formel berechneten Wert gut übereinstimmt.

(5) Aus salzkryoskopischen Untersuchungen folgt, daß das Tantalatanion 5 Tantalatome enthält.

(6) Messungen der Leitfähigkeit beim Versetzen von Alkalitantalatlösungen mit 0,1*n* Schwefelsäure zeigen, daß eine siebenbasische Säure vorliegen muß.

(7) Nach diesen übereinstimmenden Resultaten sind die untersuchten Salze als Alkali-Pentatantalate aufzufassen. Sie leiten sich von einer auch strukturell einfach

zu formulierenden Pentatantalsäure $H_7(Ta_5O_{16})\cdot aqu.$ ab, in der die vier Sauerstoffatome der Orthotantalsäure $H_3TaO_4$ durch $(TaO_4)^{3-}$-Gruppen ersetzt zu denken sind.

(8) Anzeichen für die Existenz einer Hexa- oder Dekatantalsäure sind aus unseren Untersuchungen nicht ersichtlich. Der von F. WINDMAISSER vermutete Homogenitätsbereich zwischen Hexa- und Pentatantalat dürfte sich damit als unbegründet erwiesen haben!

Von dem Ergebnis der Arbeit von I. LINDQUIST und B. ARONSSON[6] nehmen wir nach eingehender Prüfung des gegebenen Materials ausdrücklich Abstand. Diese Autoren lassen über Einzelheiten der Analysenmethode zur Bestimmung des Molverhältnisses $K_2O : Ta_2O_5 : H_2O$ in dem von ihnen dargestellten Kaliumtantalat nichts verlauten; wie wir uns im Rahmen unserer Arbeit überzeugen konnten, ist jedoch gerade dieser Punkt von ausschlaggebender Bedeutung! Die Tatsache, daß alle von uns dargestellten und analysierten Alkalitantalate ausnahmslos als Pentatantalate aufzufassen sind, daß wir darüber hinaus niemals ein Alkalitantalat erhalten konnten, welches einem Hexatantalat auch nur annähernd entsprochen hätte, weiterhin die Ergebnisse verschiedener, vielfach erprobter Methoden zur Bestimmung der Molekulargröße des Tantalatanions, die sämtlich zu vollkommen übereinstimmenden Aussagen führen, lassen keine Zweifel an der ausschließlichen Existenz des Pentatantalatanions in wässriger Lösung zu.

Wir danken den Firmen Siemens & Halske, Berlin, und Telefunken, Berlin, für die freundliche Überlassung von Tantalmetall. Die Durchführung dieser Arbeit wurde uns durch die Gewährung von ERP-Mitteln ermöglicht.

## Separation of the Lanthanides by Ion Exchange with Alpha-hydroxy Isobutyric Acid

(*Received* 13 *April* 1956)

SEPARATION factors have been reported recently for the tripositive transplutonium actinide elements on elution from a cation exchange resin column with a solution of ammonium α-hydroxy isobutyrate.[1] Table 1 is a summary of the separation factors, $\alpha_0$, of the lanthanide elements expressed relative to gadolinium. These data were obtained from elution volumes after subtraction of the free column volume. Curium is included in order that the relative positions of the lanthanides and actinides may be compared by using the data in ref. 1. The probable error in these separation factors is of the order of 5%.

TABLE 1

| Element | $\alpha_0$ | Element | $\alpha_0$ |
|---|---|---|---|
| La | 34·10 | Tb | 0·49 |
| Ce | 16·70 | Dy | 0·26 |
| Pr | 10·45 | Ho | 0·16 |
| Nd | 6·60 | Er | 0·13 |
| Pm | 4·10 | Tm | 0·10 |
| Sm | 2·25 | Yb | 0·075 |
| Eu | 1·40 | Lu | 0·055 |
| Gd | 1·00 | Y | 0·25 |
| | | Cm | 3·45 |

A Dowex-50 X-12 (400 + mesh) resin bed 5 cm × 0·2 cm was used in a column of the type previously described.[2] The elution was performed at 87°C at a flow-rate of 1·0 ml/cm²/min, although preliminary experiments indicate that elution at 25°C does not decrease the separation factors more than 10%. The large separation factors made it necessary to perform a number of elutions using various combinations of three to five adjacent lanthanides (Fig. 1). The eluting solutions ranged

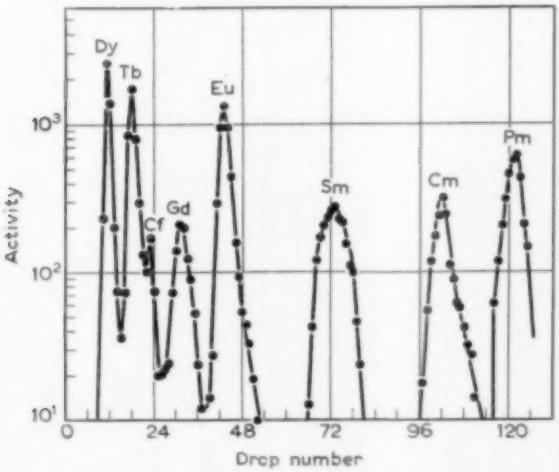


FIG. 1

from 0·2 M in α-hydroxy isobutyric acid pH 4·0 for lutetium-ytterbium-thulium separations to 0·4 M pH 4·6 for neodymium-praseodymium-cerium-lanthanum. The pH necessary to elute an ion in a desired volume was determined for a 0·4 M solution of isobutyrate from a pH vs. drop number curve (ref. 1, Fig. 2) by using the separation factor relative to curium. In order to minimize pH sensitivity, it was desirable to use solutions in a pH range of 4·2 to 4·8. If for a particular separation the curve indicated the choice of a 0·4 M solution of pH lower than 4·2, concentrations of 0·3 M or 0·2 M were used instead. Since the concentration of free isobutyrate ion determines the elution volume, the acid-constant expression was used to calculate the pH necessary to give the same isobutyrate ion concentration as the 0·4 M pH combination obtained from the curve. The value for the $K_a$ at 25°C ($1{\cdot}1 \times 10^4$) could be used in this calculation with satisfactory results.

Table 2 is a comparison of the separation factors relative to samarium for several rare earths with ethylenediamine tetracetic-acid (EDTA), citric-acid, and lactic-acid solutions as reported by MAYER and FREILING.[3] The data for α-hydroxy isobutyric acid has been entered in the last column.

TABLE 2

| R.E. | 0·026 M EDTA 0·4 ml/cm²/min | 0·5 M citrate 0·4 ml/cm²/min | 0·24 M lactate 3·5 ml/cm²/min | 0·3 M isobutyrate 2·0 ml/cm²/min |
|---|---|---|---|---|
| Sm | 1·00 | 1·00 | 1·00 | 1·00 |
| Eu | 1·57 | 1·20 | 1·28 | 1·60 |
| Tb | 5·18 | 1·87 | 2·22 | 4·60 |
| Y | | 2·56 | 4·08 | 9·00 |

While the separation factors for the α-hydroxy isobutyric acid are comparable to those for EDTA, the flow rate with the former is five times greater. This was the flow-rate which gave a 10% value for the full width at half maximum for the elution peaks. The data are for the band-elution method rather than the band-displacement method usually used with EDTA.[4] The solubility of the lanthanum salt of α-hydroxy isobutyric acid was determined to be 70 g/l. (0·5 N) at 19°C and pH 5·8, which is greater than the reported solubility of the lanthanum salt of EDTA.[5] These considerations suggest that α-hydroxy isobutyric acid may be superior to EDTA even for the band-displacement method.

A factor which seems to have been ignored in previous work is the possibility of dimeric diester formation with the α-hydroxy carboxylic acids. Since the presence of the dimer in these acids will lower the actual concentration of free acid, the column calibration data may vary from batch to batch of C.P. acid. That such dimer formation can occur may be demonstrated with lactic acid by a simple test for esters.[6] By saponifying a portion of the lactic acid with sodium hydroxide, then removing the $Na^+$ with a $H^+$ form Dowex-50 column, lactic acid which gave a negative dimer test was obtained. The same separation factors were obtained with this acid, but the elution volume was one-forth that required by solutions of the same concentration (as determined by alkali titration) and pH of the untreated acid. It could be calculated that approximately 30% of the lactic acid was dimerized. This might be due to a distillation step in the final purification industrially. Neither glycolic nor α-hydroxy isobutyric acid showed a positive dimer test. Being crystalline, they probably were purified by recrystallization, which avoids the conditions (very hot, concentrated solutions) necessary for dimer formation.

The assistance of ROBERTA GARRETT in this work and the helpful suggestions of B. G. HARVEY, R. M. MCCREADY, and S. G. THOMPSON are gratefully acknowledged.

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[1] G. R. CHOPPIN, B. G. HARVEY, and S. G. THOMPSON *J. Inorg. Nucl. Chem.* **2**, 66 (1956).
[2] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN, and G. T. SEABORG *J. Amer. Chem. Soc.* **76**, 6229 (1954).
[3] S. W. MAYER and E. C. FREILING *J. Amer. Chem. Soc.* **75**, 5647 (1953).
[4] F. H. SPEDDING and E. J. WHEELWRIGHT *J. Amer. Chem. Soc.* **75**, 2529 (1953).
[5] H. VON BRINTZINGER, H. T. THIELE, and URSULA MÜLLER *Z. Anorg. Chem.* **251**, 285 (1943).
[6] R. M. MCCREADY and R. M. REEVE *Agri. and Food Chem.* **3**, 260 (1955).

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## The Separation of Zirconium and Protoactinium by an Anion-exchange Column

(*Received* 20 *April* 1956)

In a recent paper, Maddock and Pugh[1] described conditions for the separation of zirconium and protoactinium by employing chloride-complex formation on both Dowex-2 and Amberlite IRA-400 anion-exchange resins. Similar investigations at this laboratory with Dowex-1 resin supplement these data.

The method used for the determination of $K_d$ was as follows: A sample of oven-dried Dowex-1 × 10 resin, 200–400 mesh, was weighed in a 4-oz polyethylene-capped glass vial. A 25-$\mu$l aliquot of the activity ($Pa^{231}$ or $Zr^{95}$) and 1 ml of HCl in the desired concentration were added to the resin. The vials were then agitated for two hours on a mechanical shaker. At the end of this time the mixed

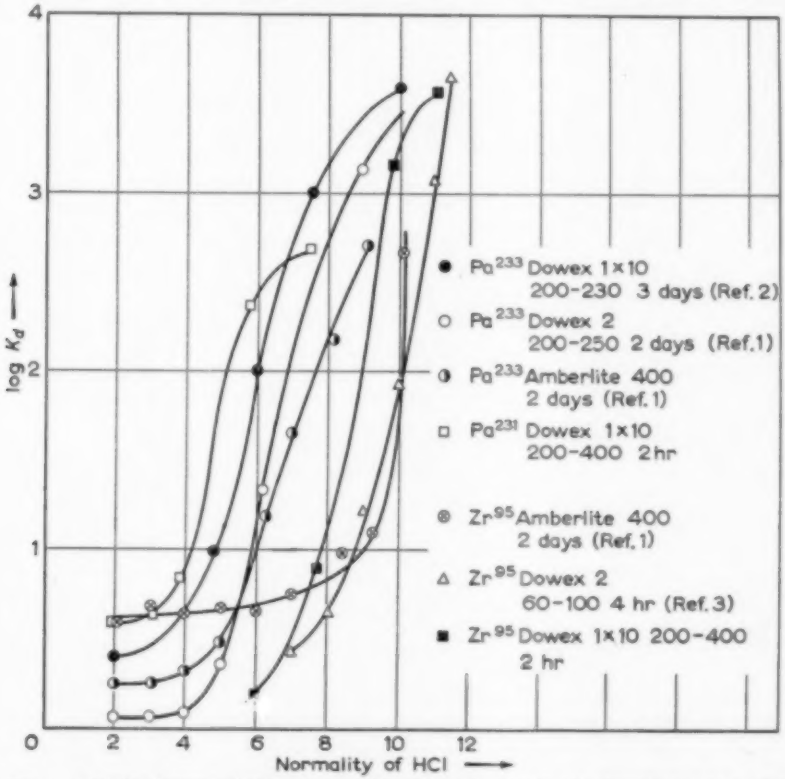


Fig. 1.—Relation between distribution coefficient $K_d$ and molarity of hydrochloric acid for $Pa^{231}$ and $Zr^{95}$ on different anion-exchange resins.

phases were filtered through glass wool, and 100-$\mu$l and 250-$\mu$l aliquots were taken from the filtrate. The 100-$\mu$l aliquot was titrated with standardized NaOH to determine the acid concentration. The 250-$\mu$l aliquot was evaporated on a platinum disc. The disc was flamed and counted with either an alpha $2\pi$ scintillation counter or a methane end-window proportional beta counter. The value of $K_d$ was then calculated from the difference of the initial activity and the total activity found in the aequeous phase.

$$K_d = \frac{\text{(initial activity-activity in aqueous phase)/gram oven-dried resin}}{\text{activity/ml of solution}}$$

The normal procedure for the separation of elements in this laboratory involves ion-exchange

chromatography, which is accomplished through the use of resin columns 1·3 cm diameter and 1·5 to 3·0 cm long, with a flow-rate of 1 to 2 ml/min. The elution is therefore made under non-equilibrium conditions. Since it was desired to obtain $K_d$ values for the conditions approximating those established on the columns, the phases were agitated for only two hours.

The results of the measurements are shown in Fig. 1. Our values for $K_d$ obtained under the above conditions are compared to those reported by MADDOCK and PUGH.[1]

Further studies are in progress at this laboratory on the elements Nb, U, Np, and Pu in various oxidation states for both equilibrium and nonequilibrium distribution between Dowex-1 resin and HCl. The results of this work will be reported at a later date.

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[1] A. G. MADDOCK and (the late) W. PUGH *J. Inorg. Nucl. Chem.* **2**, 114 (1956).
[2] K. A. KRAUS and G. E. MOORE *J. Amer. Chem. Soc.* **72**, 4293 (1950).
[3] E. H. HUFFMAN, G. M. IDDINGS, and R. C. LILLY *J. Amer. Chem. Soc.* **73**, 4474 (1951).

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## Erratum

I. LINDQVIST and A. NIGGLI: The crystal structure of antimony trichloride. *J. Inorg. Nucl. Chem.* **2**, 345 (1956).

THE correct parameters in the abstract are

4 Sb in 4(*c*) with $x = 0{\cdot}025$ and $y = 0{\cdot}995$

4 $Cl_I$ in 4(*c*) with $x = 0{\cdot}671$ and $y = 0{\cdot}077$

8 $Cl_{II}$ in 8(*d*) with $x = 0{\cdot}132$, $y = 0{\cdot}176$ and $z = 0{\cdot}066$

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# NEUTRON CROSS-SECTION OF $Re^{188}$ AND HALF-LIFE OF $Re^{189}$*

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**Abstract**—The irradiation of a rhenium sample for 16 days in an average thermal neutron flux of $1{\cdot}80 \times 10^{14}$ n/cm² sec failed to produce observable quantities of second-order Re activities. From an upper limit estimated for the activity of all residual long-lived species it is concluded either that the absorption cross-section of $Re^{188}$ is unusually small or that the half-life commonly assumed for $Re^{189}$ is in error.

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## 1. INTRODUCTION

THE results of a highly intense thermal neutron irradiation of natural rhenium are inconsistent with a $Re^{189}$ half-life of 150–240 days.[1–3] Previous studies of reactor-irradiated Re revealed the presence of three activities, a 40-day, a 150-day, and a >5-year activity, which were resolved after the 17-hour $Re^{188}$ and the 91-hour $Re^{186}$ had decayed.[1, 2] The 40-day activity was identified as $Re^{184}$ formed by the $(n, 2n)$ reaction on $Re^{185}$. Neither of the longer-lived activities was identified, but it was suggested that one of these was probably $Re^{189}$ formed by successive neutron capture in $Re^{187}$.

Additional evidence in support of a longer-lived $Re^{189}$ isotope was presented by TURNER and MORGAN,[3] who studied the rhenium fraction isolated from tungsten bombarded by deuterons and alpha particles and found a 240-day component which they suggested could be $Re^{189}$.

On the other hand, BUTEMENT[4] suggests that a 17-min rhenium activity produced by a $(\gamma, p)$ reaction on natural osmium might be either $Re^{189}$ or $Re^{191}$. It is interesting to note that ATEN and DE FEYFER [5, 6] have also observed short-lived rhenium activities produced by fast-neutron irradiations of natural osmium.

## 2. EXPERIMENTAL

In the course of measurements of the $Re^{188}$ neutron absorption cross-section, a sample of metallic rhenium (obtained from the Jarrell-Ash Company) was irradiated for 16 days in an average thermal flux of $1{\cdot}80 \times 10^{14}$ n/cm² sec in a high-flux facility of the MTR (Materials Testing Reactor). Following the irradiation, the sample was prepared for $4\pi$ beta counting by the evaporation of the activities from a tungsten filament (under vacuum) onto thin aluminium foils (120 $\mu$g/cm²). Several samples of different activity levels were prepared, and were followed with a windowless $4\pi$ beta counter over a period of 65 days.

* Research carried out under contract with the U.S.A.E.C.

[1] M. LINDNER and J. S. COLEMAN *Phys. Rev.* **78**, 67 (1950).
[2] M. LINDNER *Phys. Rev.* **84**, 240 (1951)
[3] S. E. TURNER and L. O. MORGAN *Phys. Rev.* **81**, 881 (1951).
[4] F. D. S. BUTEMENET *Proc. Phys. Soc.* **A64**, 345 (1951).
[5] A. H. W. ATEN JR. and G. D. DE FEYFER *Physica* **19**, 1143 (1953).
[6] A. H. W. ATEN JR. and G. D. DE FEYFER *Physica* **21**, 543 (1955).

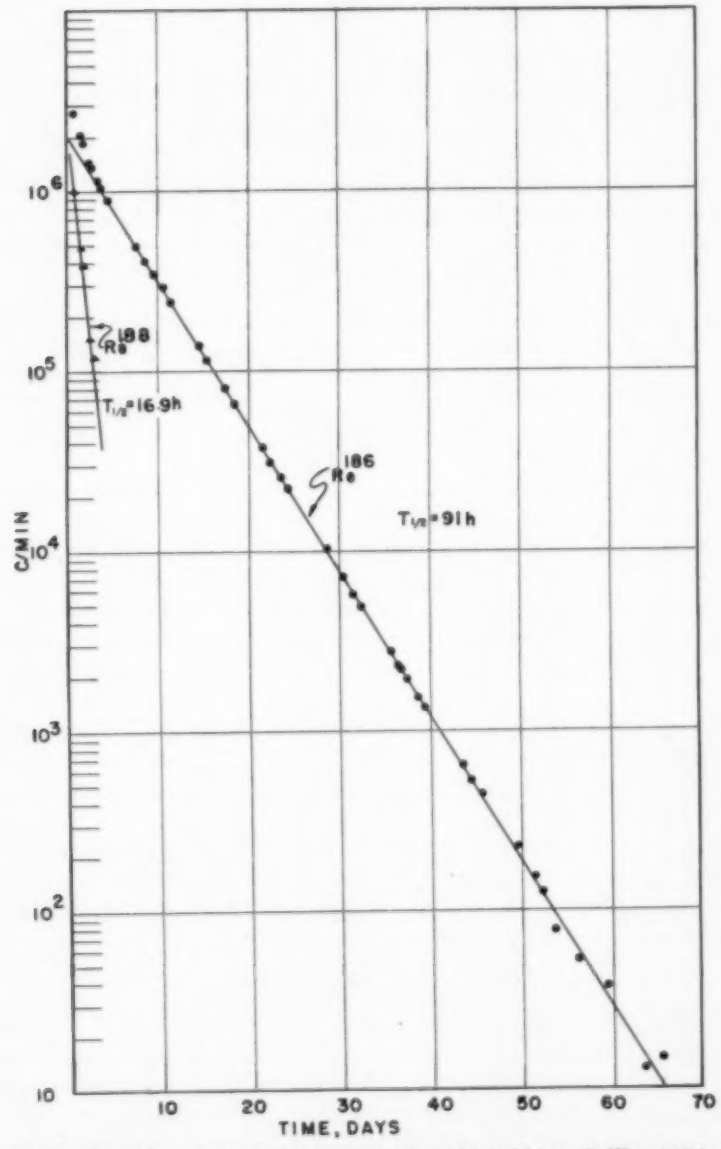


FIG. 1.—Gross decay of irradiated rhenium separated into 91-hour $Re^{186}$ and 17-hour $Re^{188}$ activities. Corrections for resolving time losses and background have been applied to the data.

Two components are apparent in the gross decay curve given in Fig. 1. The longer-lived component, decaying with a half-life of 91 hours, is that of $Re^{186}$, while the shorter-lived component, decaying with a half-life of 17 hours, is that of $Re^{188}$. After 30 days of decay, corrections for room and counter background were applied to the data shown. As can be seen from Fig. 1, the gross decay was followed until it was no longer possible to separate a net effect.

Ninety days after the irradiation an attempt was made with an end-window proportional counter (with a much lower background) to detect a difference between the gross and background counting rates. No difference was noted. With the counting statistics obtained, it was felt that a difference of 1 c/min could have been observed. Using this as an estimate for the maximum activity detected, and considering the geometry of the sample and detector, an estimate of 3 d/min may be set as an upper limit for the activity of any residual long-lived species. If the upper limit of 3 d/min is assumed to be that of the 150-day $Re^{189}$ suggested by LINDNER,[1, 2] an upper limit of the absorption cross-section of $Re^{188}$ may be made.

The ratio of the $Re^{188}$ and $Re^{189}$ activities after an irradiation of time $t$ in a thermal neutron flux of $\phi$ neutrons/cm$^2$ sec is given by

$$R = \frac{\lambda_1(\lambda_1 - \lambda_2)\,(1 - e^{-\lambda_1 t})}{\phi\sigma_1[\lambda_1(1 - e^{-\lambda_2 t}) - \lambda_2(1 - e^{-\lambda_1 t})]} \tag{1}$$

where the subscripts 0, 1, and 2 refer to $Re^{187}$, $Re^{188}$, and $Re^{189}$, respectively. Substitution of the zero-time $Re^{188}$ activity, $1{\cdot}9 \times 10^6$ d/min (from Fig. 1) and the upper limit of 3 d/min for the $Re^{189}$ activity (corrected for decay) into this expression gives an upper limit of about 2 barns for the $Re^{188}$ absorption cross-section.

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Since $Re^{188}$ is an odd proton-odd neutron nuclide, the binding energy for an additional neutron is high; hence, a much larger cross-section is anticipated. Although few cross-sections of odd-odd nuclides in this mass region have been measured, a value of the order of $10^3$ barns may be inferred from the data compiled by EVANS.[7] Such a large inconsistency between nuclear systematics and experiment is difficult to reconcile.

If a value of $10^3$ barns is assumed for the $Re^{188}$ cross-section, then it is reasonably certain that $Re^{189}$ with a half-life of 150 days would have been observed. Since it was not detected, the validity of the half-life commonly assumed for $Re^{189}$, and consequently the mass assignment, is questioned. If the half-life of $Re^{189}$ is either long, of the order of 100 years, or short, of the order of days, its presence would not have been detected in these measurements. Thus, either the cross-section of $Re^{188}$ is unusually small, which in itself is of interest in the study of cross-section systematics, or the half-life of $Re^{189}$ is too short (less than 5 days) or too long (greater than 100 years) to be observed in this manner.

On the basis of this evidence it seems more likely that, of the two long-lived activities described by LINDNER,[1, 2] the >5-year activity should be associated with $Re^{189}$. On the other hand, the evidence is also consistent with a much shorter half-life such as that observed by BUTEMENT[4] and by ATEN and DE FEYFER.[5, 6]

It is hoped that these findings will stimulate additional experimentation directed at establishing the $Re^{189}$ half-life with greater certainty. This nuclide should be producible in measurable quantities by either of the reactions, $Os^{190}(\gamma, p)Re^{189}$, and $Os^{189}(n, p)Re^{189}$. Separated isotopes should be used in these bombardments to avoid complications from extraneous activities.

[7] J. E. EVANS *Phys. Rev.* **96**, 849 (1954).

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# HALF-LIVES OF $Ce^{144}$, $Co^{58}$, $Cr^{51}$, $Fe^{55}$, $Mn^{54}$, $Pm^{147}$, $Ru^{106}$, AND $Sc^{46}$

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**Abstract**—Half-lives have been obtained for a number of radionuclides by following the decay of purified samples over periods of time as long as six years. The data were treated by the method of least squares. The half-lives are 284·5 ± 1·0 days for $Ce^{144}$, 71·3 ± 0·2 days for $Co^{58}$, 27·8 ± 0·1 days for $Cr^{51}$, 2·60 ± 0·02 years for $Fe^{55}$, 278 ± 5 days for $Mn^{54}$, 2·66 ± 0·02 years for $Pm^{147}$, 366·6 ± 0·9 days for $Ru^{106}$, and 84·1 ± 0·3 days for $Sc^{46}$.

IN the course of our work, the half-lives of $Ce^{144}$, $Co^{58}$, $Cr^{51}$, $Fe^{55}$, $Mn^{54}$, $Pm^{147}$, and $Sc^{46}$ have been determined with considerable precision. Purified samples were mounted on holders and counted at intervals in the same counter under reproducible conditions. All of the samples except $Mn^{54}$ were counted with an end-window methane flow proportional counter, Nucleometer; the $Mn^{54}$ sample was counted with an end-window Geiger-Müller counter. At least 10,000 counts were taken each time except for the points with very low counting-rates near the end of the decay curves. A uranium beta-counting standard was counted with each determination. Normally, the standard did not show more than statistical variation; if it did, the data taken at that time were discarded. Except for the $Co^{58}$ samples, where the decay curves showed a small amount of long-lived $Co^{60}$, the decay curves did not deviate significantly from a straight line.

The half-lives were calculated and the standard deviations determined by the method of least squares.[1] The results are summarized in Table 1. The errors given are the least squares standard deviations of the half-life. These standard deviations may not include all of the error, but we know of no systematic error that should

TABLE 1.—HALF-LIVES DETERMINED BY LEAST-SQUARES ANALYSIS OF DATA

| Nuclide | Half-life | Least-squares standard deviation | Number of half-lives followed | Number of points |
|---|---|---|---|---|
| $Ce^{144}$ | 284·5 days | 1·0 days | 8 | 206 |
| $Co^{58}$ | 71·3 days | 0·2 days | 7 | 58 (2 samples) |
| $Cr^{51}$ | 27·8 days | 0·1 days | 10 | 51 (3 samples) |
| $Fe^{55}$ | 2·60 years | 0·02 years | 1·8 | 64 |
| $Mn^{54}$ | 278 days | 5 days | 2 | 24 |
| $Pm^{147}$ | 2·66 years | 0·02 years | 1·8 | 55 |
| $Ru^{106}$ | 366·6 days | 0·9 days | 5 | 49 |
| $Sc^{46}$ | 84·1 days | 0·3 days | 8 | 27 |

* Operated by the General Electric Company for the US Atomic Energy Commission.

[1] W. J. YOUDEN *Statistical Methods for Chemists*, pp. 40–47, John Wiley and Sons, New York (1951).

be added to them. Since the standard counted with all the samples is a beta standard, there is a possibility that some change in the X-ray counting efficiency might have occurred without being detected.

The purification of the samples, additional details concerning the counting, and comparisons with other work are given below under the individual nuclides.

*$Ce^{144}$*. The $Ce^{144}$ sample was radiochemically isolated from fission products[2, 3] after a decay of over one year, so that the sample was free of $Ce^{141}$. The counting rate of the single sample was followed for six and one-half years, giving a half-life of $284{\cdot}5 \pm 1{\cdot}0$ days. The present determination can be compared with values of $282 \pm 3$ days obtained from the first 560 days decay of the same sample,[4] and with literature values of 275 days,[5] $290 \pm 30$ days,[6] and 310 days.[7]

*$Co^{58}$*. The $Co^{58}$ was prepared by irradiating spectroscopically pure nickel powder inside a hollow uranium slug in the Brookhaven Reactor. The $Co^{58}$ is produced by an $n, p$ reaction on the $Ni^{58}$ in the sample. For one sample, cobalt was chemically separated from the irradiated nickel by extracting $Co(CNS)_3$ from an aqueous solution into 50% amyl alcohol–50% ethyl ether solution, and by precipitation of the cobalt as $K_3Co(NO_2)_6$. The irradiated nickel, without purification, was followed for a second sample. Both samples decayed to a long-lived tail due to $Co^{60}$ from $Ni^{60}$ $(n, p)$, which was about 0·1% of the initial $Co^{58}$ activity. The half-lives of both samples were the same within the standard deviation. Our half-life of $71{\cdot}3 \pm 0{\cdot}2$ days can be compared with values of $72 \pm 4$ days[8] and 72 days[9] in the literature.

*$Cr^{51}$*. The $Cr^{51}$ was produced by irradiating spectroscopically pure $Cr_2O_3$ in the Chalk River reactor. After irradiation, the chromium was purified either by extraction of peroxy chromic acid into ethyl ether or by distillation of $CrO_2Cl_2$, or both, followed by precipitation of the chromium as $BaCrO_4$. All three samples decayed to the counter background and showed the same half-life within the standard deviation. Our value of $27{\cdot}8 \pm 0{\cdot}1$ days can be compared with literature values of $27{\cdot}75 \pm 0{\cdot}3$ days,[10] and $26{\cdot}5 \pm 1{\cdot}0$ days.[11]

*$Fe^{55}$*. The $Fe^{55}$ sample was obtained from the Isotopes Division of the Oak Ridge National Laboratory. It was produced, with very little $Fe^{59}$, by irradiating enriched $Fe^{54}$ in the Oak Ridge reactor. The counting was started after the $Fe^{59}$ had decayed. The half-life obtained over a period of 5 years is $2{\cdot}60 \pm 0{\cdot}02$ years (see Fig. 1). This value is appreciably lower than the value of about 3·0 years obtained graphically from the first year of the decay curve;[4] the discrepancy is due mainly to the initial point (at 0 days) which is low. Our present value is also lower than the half-life of 2·94 years obtained by BROWNELL and MELETSKOS.[12]

[2] R. P. SCHUMAN Paper 293, p. 1692, Radiochemical Studies: The Fission Products. *National Nuclear Energy Series IV*, 9, McGraw-Hill Book Co., Inc., New York (1951).
[3] W. F. BOLDRIDGE and D. N. HUME Paper 294, p. 1693, Radiochemical Studies: The Fission Products. *National Nuclear Energy Series IV*, 9, McGraw-Hill Book Co., Inc., New York (1951).
[4] R. P. SCHUMAN and A. CAMILLI *Phys. Rev.* **84**, 158 (1951).
[5] W. H. BURGUS, L. WINSBERG, J. A. SEILER, and W. RUBINSON Paper 184, p. 1195, Radiochemical Studies: The Fission Products. *National Nuclear Energy Series IV*, 9, McGraw-Hill Book Co., Inc., New York (1951).
[6] F. JOLIOT *Compt. Rend.* **218**, 733 (1944).
[7] H. J. BORN and W. SEELMANN-EGGEBERT *Naturwiss* **31**, 201 (1943).
[8] D. C. HOFFMAN and D. S. MARTIN *J. Phys. Chem.* **56**, 1097 (1952).
[9] J. J. LIVINGOOD and G. T. SEABORG *Phys. Rev.* **60**, 913 (1941).
[10] W. S. LYON *Phys. Rev.* **87**, 1126 (1952).
[11] H. WALKE, F. C. THOMPSON, and J. HOLT *Phys. Rev.* **57**, 171 (1940).
[12] G. L. BROWNELL and C. J. MELETSKOS *Phys. Rev.* **80**, 1102 (1950).



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*$Mn^{54}$*. The $Mn^{54}$ sample was produced by an *n*, *p* reaction on $Fe^{54}$ in iron irradiated in a hollow uranium slug in the Brookhaven reactor. The manganese was purified from iron and impurities by $MnO_2$ precipitations from acid solutions. The sample was followed for decay, using an argon-ethanol filled Geiger tube. Our half-life of $278 \pm 5$ days can be compared with literature values of $324 \pm 11$ days,[13] $291 \pm 1$ days,[14] and $290 \pm 10$ days.[14]

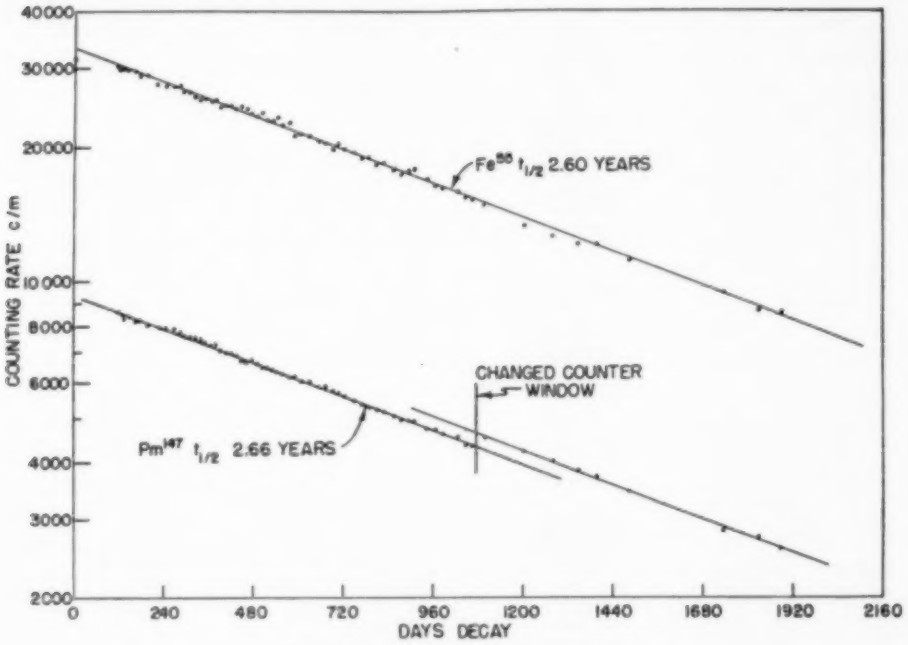


FIG. 1.—Decay curve of $Fe^{55}$ and $Pm^{147}$.

*$Pm^{147}$*. The $Pm^{147}$ sample was isolated from fission products by a method which separates the rare earths, other than cerium, from the other fission products and cerium.[3] Before the decay curve was started, the sample had decayed several years, so only the long-lived rare-earth fission products remained. The only fission products other than $Pm^{147}$ that would be present are 73-year $Sm^{151}$, which, because of the very low-energy beta rays, would not count under the conditions used, and 1·7-year $Eu^{155}$, which has a low fission yield,[15] about 1% that of $Pm^{147}$, and which is counted with somewhat lower efficiency than $Pm^{147}$. In calculating the half-life, no correction was made for the $Eu^{155}$ impurity. The half-life determined over a 5 year decay period was $2{\cdot}66 \pm 0{\cdot}02$ years (see Fig. 1). This value can be compared with a half-life of $2{\cdot}6 \pm 0{\cdot}2$ years obtained from the first-year decay of the same sample,[4] and half-lives of 2·26 years[16] and $2{\cdot}52 \pm 0{\cdot}08$ years[17] obtained by mass analysis.

*$Ru^{106}$*. The $Ru^{106}$ sample was obtained from the Isotopes Division of the Oak

[13] G. H. STAFFORD and L. H. STEIN *Nature* **172**, 1103 (1953).
[14] E. W. BACKOFEN and R. H. HERBER *Phys. Rev.* **97**, 743 (1955).
[15] J. M. SIEGEL *J. Amer. Chem. Soc.* **68**, 2411 (1946).
[16] M. G. INGHRAM, R. J. HAYDEN, and D. C. HESS *Phys. Rev.* **79**, 271 (1950).
[17] E. A. MELAIKA, M. J. PARKER, J. A. PETRUSKA, and R. H. TOMLINSON *Canad. J. Chem.* **33**, 830 (1955).

Ridge National Laboratory. After sufficient time so that 42-day $Ru^{103}$ had decayed, the ruthenium was purified, then electroplated on a platinum plate. Our half-life of 366·6 ± 0·9 days agrees well with the literature value of 1·0 years.[18, 19]

*$Sc^{46}$*. The $Sc^{46}$ sample was produced by an *n*, *p* reaction on spectroscopically pure titanium oxide irradiated in the Chalk River reactor. The scandium was separated from the titanium and purified by thenoyltrifluoroacetone extractions. Our half-life of 84·1 ± 0·3 days can be compared with literature values of 85 ± 1 days,[20] and 84 days.[21]

*Acknowledgements*—We wish to thank Dr. D. L. DOUGLAS, who separated and purified the $Sc^{46}$ sample, and Dr. B. F. RIDER and Mrs. H. C. HENDRICKSON, who helped with the calculations on $Ce^{144}$. We also wish to thank the operators of the Chalk River and Brookhaven reactors for irradiating samples and the Isotopes Division of the Oak Ridge National Laboratory for supplying some of the samples.

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[18] W. SEELMANN-EGGEBERT *Naturwiss.* **33**, 279 (1946).
[19] L. E. GLENDENIN and E. P. STEINBERG *Radiochemical Studies: The Fission Products.* National Nuclear Energy Series IV, 9, paper 103, p. 793, McGraw-Hill Book Co. Inc., New York (1951).
[20] H. WALKE, E. J. WILLIAMS, and G. R. EVANS *Proc. Roy. Soc.* **171A**, 360 (1939).
[21] F. T. PORTER and C. S. COOK *Phys. Rev.* **81**, 640 (1951).

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# THE RELATIVE STABILITIES OF SOME MOLECULAR ADDITION COMPOUNDS OF BORON[1]

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(*Received* 23 *May* 1956)

**Abstract**—Using boron trifluoride as a reference acceptor molecule, the methyl derivatives of oxygen, sulphur and selenium have an order of electron-pair donor power: O > S > Se. With both borine and trimethylborine, however, the order of co-ordination is S > Se, O. Moreover, the adducts $(CH_3)_2S{\cdot}BH_3$ and $(CH_3)_2Se{\cdot}BH_3$ are more stable than their boron trifluoride analogues. The weakness of boron trifluoride as an acid was further demonstrated by its quantitative displacement by diborane from the complex $(CH_3)_3P{\cdot}BF_3$. In Group V*b* the order of co-ordination of methyl derivatives towards $BH_3$ is apparently P > N > As > Sb, compared with the order N > P > As > Sb shown by all other Group-III*b* acceptor molecules so far investigated. Possible explanations for these observations are discussed.

## 1. INTRODUCTION

As a consequence of studies carried out by a number of workers it is now recognized that the electron-donor bonding power of the elements of Groups V*b* and VI*b* does not always decrease with increasing atomic size. This has necessitated a modification of ideas concerning the nature of the bonding in some compounds once thought by most to be satisfactorily described in terms of the classical co-ordinate link. The majority of complexes inadequately described by the lone-pair theory of co-ordination are formed by a few transition metals. However, the chemistry of some of the compounds formed by III*b* elements, and of boron in particular, provides several other examples of unusual relative stabilities, the explanation of which may require applying as many concepts as the modern theory of valence can suggest.

The work described here was carried out in order to extend our knowledge of borine-type adducts, with the special object of preparing compounds likely to display unexpected stability relationships when viewed in terms of what is so far known about order of co-ordination of ligands to III*b* atoms.

Several techniques have been used for the assignment of relative electron-pair donor power of the atoms of Group V and Group VI. The most satisfactory method involves study in the gas phase of the thermal dissociation of the complex. Knowledge of the variation of dissociation with temperature permits thermodynamic constants to be evaluated, and a quantitative measure of the strength of the metal-ligand bond is thereby obtained. It is unfortunate that many complexes are either too stable or too unstable for the application of this method.

Fortunately, for many purposes it is sufficient to establish relative stabilities only qualitatively. The use of displacement reactions supplies this information. Although sometimes complicated by lattice energy and volatility effects, the method has proven

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[1] This paper represents a part of the work submitted by WILLIAM A. G. GRAHAM to the Graduate School of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

useful for the more stable complexes. Furthermore calorimetric procedures have recently been developed for the determination of the heats of formation *in solution* of molecular addition compounds.[2] Of these methods, gas phase dissociation studies and displacement reactions have been the most widely used.

It is important also to note that for complexes of low stability, it has long been customary to infer relative stabilities from relative volatilities. The following rule has been formulated:[3] "... of two addition compounds of closely similar structure and molecular weight, the less stable exhibits the higher saturation pressure." For addition compounds differing in molecular weight, it would be expected that the heavier would be the less volatile. If instead the heavier is found to be more volatile, this is taken to indicate that it is also more highly dissociated.

Thus DAVIDSON and BROWN,[4] using trimethylaluminium as a reference acid in the LEWIS[5] sense, have examined the stability of the adducts $(CH_3)_3N{\cdot}Al(CH_3)_3$, $(CH_3)_3P{\cdot}Al(CH_3)_3$, $(CH_3)_2O{\cdot}Al(CH_3)_3$, and $(CH_3)_2S{\cdot}Al(CH_3)_3$. Furthermore, COATES[6] has studied the complex $(CH_3)_2Se{\cdot}Al(CH_3)_3$, as well as molecular addition compounds obtained by treating the acceptor molecule trimethygallium with the methyl alkyls of V*b* and VI*b* elements.

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The experimental results of these workers demonstrated that towards trimethylaluminium stability decreased in the order N > P, and also O > S > Se. With the common electron-pair acceptor trimethylgallium the order of co-ordination to Group-V alkyls was similar, *viz.*: N > P > As > Sb, but in Group VI the order was O > Se > S ~ Te. Both in the case of trimethylaluminium and trimethylgallium, however, oxygen was found to be a better electron-pair donor than sulphur, and nitrogen a better donor than phosphorus. This has been contrasted[7, 8] with the reverse behaviour of certain transition metals. However, BURG and WAGNER,[9] made the important observation that $(CH_3)_2S{\cdot}BH_3$ was more stable than $(CH_3)_2O{\cdot}BH_3$, showing that towards borine the bonding power of sulphur in dimethylsulphide was greater than that of oxygen in dimethylether. The implication of this discovery to the co-ordination chemistry of Group III has been briefly mentioned elsewhere.[10, 11] Thus in terms of the behaviour of aluminium and gallium towards oxygen and sulphur as donors the behaviour of boron, as borine at least, is anomalous. Since the strength of a ligand-metal bond depends in part on the substituents on both the ligand and the metal we were prompted to prepare a number of new $BX_3$-type adducts, and re-examine more closely some borine complexes already reported.

## 2. EXPERIMENTAL

### *Apparatus and Materials*

The work described here was carried out in a high-vacuum system of conventional design. Saturated vapour pressures, and gas phase dissociations of the complexes were studied in a tensimeter.[12]

[2] H. C. BROWN and R. H. HOROWITZ *J. Amer. Chem. Soc.* **77**, 1730 (1955).
[3] H. C. BROWN and H. PEARSALL *ibid.* **67**, 1765 (1945).
[4] N. DAVIDSON and H. C. BROWN *ibid.* **64**, 316 (1942).
[5] G. N. LEWIS *J. Franklin Inst.* **226**, 293 (1938).
[6] G. E. COATES *J. Chem. Soc.* 2003 (1951).
[7] R. S. NYHOLM *Reviews of Pure and Applied Chem.* **4**, 15 (1954).
[8] D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL, and L. E. SUTTON *J. Chem. Soc.* 332 (1954).
[9] A. B. BURG and R. I. WAGNER *J. Amer. Chem. Soc.* **76**, 3307 (1954).
[10] F. G. A. STONE *Quart. Rev.* **9**, 174 (1955).
[11] W. A. G. GRAHAM and F. G. A. STONE *Chem. and Ind.* 319, (1956).
[12] A. B. BURG and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **59**, 780 (1937).

Temperatures were measured with vapour-tension thermometers, or by a mercury thermometer calibrated by the National Bureau of Standards. Infra-red spectra were recorded using a Model 21 Perkin Elmer double beam spectrometer, and a 4 cm gas cell. Hydrogen gas formed in a few of the experiments was collected in a gas burette by means of an automatic Sprengel pump. Its purity was checked by ignition over copper oxide at 700°.

The diborane used in this investigation had vapour tensions very close to the values reported in the literature, *e.g.* 224·7 mm at −111·9°, literature[13] value 225·0 mm at −111·9°. Trimethylborine was purified through its trimethylamine complex followed by displacement with a deficiency of boron trifluoride. The vapour tension was 85·6 mm at −63·5°; STOCK and ZEIDLER[14] report the same value at this temperature. The boron trifluoride used had a vapour tension of 305 mm at −111·8°. Of the donor molecules employed in this work, the purification of trimethylamine trimethylphosphine, and dimethylether presented no difficulty and the samples used had vapour tensions in agreement with those reported in the literature. Commercially available dimethylsulphide, however, was treated with a mixture of sodium and copper shot,[15] and then fractionated until a tensimetrically homogeneous sample was obtained with $p$ = 167 mm at 0° (literature[4] 167 mm). Dimethylselenide was prepared from elemental selenium by the method of BIRD and CHALLENGER[16] In our hands, the method yielded a grossly impure product. The crude dimethylselenide was transferred to the vacuum system, and a tensimetrically homogeneous product was obtained after prolonged treatment with sodium wire.

Analysis gave the following percentage composition: C, 22·08; H, 5·36; Se, 72·49; Theory for $(CH_3)_2Se$: C, 22·03; H, 5·55; Se, 72·42.

### *Characterization of Dimethylselenide*

Since vapour tensions for this compound do not seem to have been recorded, the observed values are given in Table 1.

TABLE 1.—VAPOUR TENSIONS OF LIQUID $(CH_3)_2Se$

| $t$, °C | 7 | 11 | 15 | 20 | 25 | 30 | 35 | 40 |
|---|---|---|---|---|---|---|---|---|
| $P_{mm}$ (obsd) | 99·4 | 119·9 | 144·8 | 180·6 | 223·5 | 274·0 | 333·7 | 402·8 |
| $P_{mm}$(calcd) | 100·2 | 120·8 | 144·5 | 180·3 | 222·8 | 273·5 | 333·4 | 403·6 |

The vapour tensions shown in Table 1 determine the equation $\log P_{mm} = 7{\cdot}747 - 1610/T$, whence one calculates the boiling point as 57·7° and the Trouton constant as 22·2 cal deg.$^{-1}$ mole$^{-1}$. The melting point of dimethylselenide was −87·2° (Stock magnetic plunger method).

### *Preparation and Study of Complexes*

*Dimethylether-Trimethylborine.* Dimethylether was treated with an equal volume of trimethylborine. The volumes in the gas phase at room temperature were found to be additive. Furthermore when the mixture was cooled to −78° the pressure above the liquid was only slightly less (6 per cent) than that calculated using RAOULT's law. It may be concluded that $(CH_3)_2O{\cdot}B(CH_3)_3$ does not form down to −78°.

*Dimethylsulphide-Trimethylborine.* A 19·6 c.c.* sample of dimethylsulphide was treated with 28·1 c.c. of trimethylborine in the tensimeter. After standing for 12 hours at −78·5°, 8·9 c.c. of trimethylborine were recovered. A white *solid* remained, with inappreciable saturation pressure at −78·5°. The molar ratio of $(CH_3)_2S$:$(CH_3)_3B$ in the solid is 1·02, corresponding to the complex $(CH_3)_2S{\cdot}B(CH_3)_3$.

* The term c.c. throughout this paper refers to volumes at S.T.P.

[13] A. B. BURG *J. Amer. Chem. Soc.* **74**, 1340 (1952).
[14] A. STOCK and F. ZEIDLER *Ber.* **54**, 531 (1921).
[15] D. W. OSBORNE, R. N. DOESCHER, and D. M. YOST *J. Amer. Chem. Soc.* **64**, 169 (1942).
[16] M. L. BIRD and F. CHALLENGER *J. Chem. Soc.* 570 (1942).

The saturation pressures of the solid reported in Table 2 determine the equation $\log P_{mm} = 11{\cdot}637 - 2358{\cdot}5/T$.

TABLE 2.—SATURATION PRESSURES OF SOLID $(CH_3)_2S{\cdot}B(CH_3)_3$

| $t$, °C | −69·7 | −66·1 | −64·4 | −61·3 | −56·5 | −54·8 |
|---|---|---|---|---|---|---|
| $P_{mm}$ (obsd) | 1·25 | 1·80 | 2·20 | 3·20 | 5·60 | 6·90 |
| $P_{mm}$ (calcd) | 1·11 | 1·77 | 2·20 | 3·21 | 5·68 | 6·89 |

Melting of the complex occurred over the range −43° to −41°.

At 24·8° and a pressure of 300·9 mm, the combined volume of the gases was 38·5 c.c., whereas the sum of the volumes of the components was 38·8 c.c. Hence dissociation of the complex in the gas phase is complete.

*Dimethylselenide-Trimethylborine.* A sample of dimethylselenide (39·9 c.c.) when treated with trimethylborine (39·9 c.c.) formed a white solid at −78°. After several hours at this temperature the pressure was 8·6 mm. At 25·0°C and 97·3 mm, the volume of the mixture reduced to standard conditions was 79·7 c.c., indicating complete dissociation in the gas phase.

*Dimethylsulphide-Borine.* Saturation pressures observed by us were very close to those already reported by BURG and WAGNER[9] It was important to verify the saturation pressures in order that the dissociation of the complex be studied well above the condensation point.

A sample of $(CH_3)_2S{\cdot}BH_3$ was prepared in the tensimeter by treating dimethylsulphide with exactly half its volume of diborane. The variation of pressure with temperature together with other data are recorded in Table 3. $K_p$ is the equilibrium constant for the reaction:

$$(CH_3)_2S{\cdot}BH_3(g) = (CH_3)_2S(g) + 1/2\ B_2H_6(g).$$

TABLE 3.—GAS-PHASE DISSOCIATION OF $(CH_3)_2S{\cdot}BH_3$

| $t$, °C | $P_{mm}$ (obsd) | $P_{mm}$ (calcd) | $\alpha$ | $K_p$ (atm.$^{\frac{1}{2}}$) | $K_p$(atm.$^{\frac{1}{2}}$) (calcd) |
|---|---|---|---|---|---|
| 40·0 | 37·66 | 27·20 | 0·769 | 0·391 | 0·390 |
| 42·0 | 38·00 | 27·37 | 0·777 | 0·411 | 0·411 |
| 44·0 | 38·33 | 27·55 | 0·783 | 0·430 | 0·434 |
| 46·0 | 38·72 | 27·72 | 0·794 | 0·463 | 0·456 |
| 48·0 | 39·05 | 27·89 | 0·800 | 0·485 | 0·480 |
| 50·0 | 39·38 | 28·07 | 0·806 | 0·508 | 0·505 |
| 52·0 | 39·66 | 28·24 | 0·809 | 0·519 | 0·530 |
| 54·0 | 40·04 | 28·41 | 0·818 | 0·558 | 0·556 |
| 56·0 | 40·42 | 28·59 | 0·828 | 0·600 | 0·583 |
| 58·0 | 40·70 | 28·76 | 0·830 | 0·613 | 0·612 |
| 60·0 | 41·02 | 28·93 | 0·835 | 0·640 | 0·641 |

A check of the dissociation pressures as the sample was cooled showed that no irreversible decomposition had taken place. The variation of $K_p$ with temperature is represented by the equation

$$\log K_p\,(\text{atm.}^{\frac{1}{2}}) = 3{\cdot}190 - 1127/T;\ \text{whence}\ \Delta F_T^\circ = 5157 - 14{\cdot}60T.$$

Therefore, for the reaction $(CH_3)_2S{\cdot}BH_3(g) = (CH_3)_2S(g) + 1/2\ B_2H_6(g)$, $\Delta H^\circ = 5{\cdot}2$ kcal.mole$^{-1}$ and $\Delta S^\circ = 14{\cdot}6$ e.u.

BURG and WAGNER[9] reported the degree of dissociation at one temperature, but this is rendered suspect by an error in their calculations. Their data also suggest that dissociation was studied only slightly above the saturation point, a procedure known to lead to error.[17]

[17] H. C. BROWN, M. D. TAYLOR, and M. GERSTEIN *J. Amer. Chem. Soc.* **66**, 431 (1944).

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*Dimethylselenide-borine.* Diborane and dimethylselenide reacted in exactly a 1 : 2 ratio at −78·5° to form a white solid, as would be expected for the formation of $(CH_3)_2Se{\cdot}BH_3$. The melting range of the addition compound was −34° to −32°. Saturation pressures of the complex are recorded in Table 4.

TABLE 4.—SATURATION PRESSURES OF LIQUID $(CH_3)_2Se{\cdot}BH_3$

| $t$, °C | 0·0 | 10·0 | 17·0 | 21·0 | 25·0 | 30·0 | 35·0 |
|---|---|---|---|---|---|---|---|
| $P_{mm}$ (obsd) | 51·4 | 82·0 | 115·4 | 138·7 | 167·2 | 207·7 | 256·9 |
| $P_{mm}$ (calcd) | 49·0 | 82·0 | 115·3 | 139·0 | 166·7 | 208·0 | 257·0 |

The saturation pressures shown in Table 4 determine the equation $\log P_{mm} = 8{\cdot}030 - 1732/T$, whence one calculates the "boiling point" as 63·2° and the Trouton constant as 23·5 cal $deg^{-1}$ $mole^{-1}$. When a sample of dimethylselenide-borine was studied in the gas phase over the temperature range 6° to 34°, the pressures observed were within experimental error those expected for complete dissociation.

*Dimethylsulphide-boron trifluoride.* A 26·5 c.c. sample of dimethylsulphide combined with 26·4 c.c. of boron trifluoride to form a solid at −78·5°, implying the formation of the molecular addition compound $(CH_3)_2S{\cdot}BF_3$. The saturation pressures of the liquid are recorded in Table 5. No irreversible decomposition of $(CH_3)_2S{\cdot}BF_3$ was observed during the experimental work.

TABLE 5.—SATURATION PRESSURES OF LIQUID $(CH_3)_2S{\cdot}BF_3$

| $t$, °C | 0·0 | 4·0 | 9·0 | 14·0 | 16·0 | 20·0 | 25·0 |
|---|---|---|---|---|---|---|---|
| $P_{mm}$ (obsd) | 45·5 | 59·0 | 82·0 | 112·6 | 127·4 | 163·1 | 217·2 |
| $P_{mm}$ (calcd) | 45·1 | 59·2 | 82·0 | 112·7 | 127·4 | 162·2 | 217·8 |

The results presented in Table 5 correspond to the equation $\log P_{mm} = 9{\cdot}806 - 2227/T$, implying a "boiling point" of 48·4° and a Trouton constant of 31·6 cal.$deg.^{-1}$ $mole^{-1}$.

In a study of the gas-phase dissociation, the extent of dissociation was found to vary from 96·2 to 97·4 per cent over the temperature range 12° to 34°. The observed increase in pressure over this range was 5·31 mm, while the increase expected for an ideal gas was 4·88 mm. This confirms that dissociation, although greater than 95 per cent, is not complete at these temperatures. The sensitivity of the equilibrium constant to the degree of dissociation as the latter approaches unity makes it impossible to obtain a reliable estimate of the enthalpy change for this dissociation.

*Dimethylselenide-boron-trifluoride.* Dimethylselenide (40·5 c.c.) was treated with boron trifluoride (65·2 c.c.) forming a solid at −78·5°. Subsequently, 25·0 c.c. of pure boron trifluoride was recovered; hence the dimethylselenide: boron trifluoride reaction ratio was just 1 : 1, corresponding to $(CH_3)_2Se{\cdot}BF_3$. The saturation pressure of dimethylselenide-boron trifluoride at −45·2° was 48·1 mm, and 398 ± 2 mm at 0°. The complex was thus considerably more volatile than $(CH_3)_2S{\cdot}BF_3$. Furthermore in the gas phase at room temperature $(CH_3)_2Se{\cdot}BF_3$ was found to be completely dissociated, the variation of pressure with temperature corresponding to that expected for an ideal gas.

## *Relative Stabilities of Some Complexes*

The relative stability of a number of addition compounds was established by the following displacement reactions:

1. $2(CH_3)_2S{\cdot}BF_3 + B_2H_6 = 2(CH_3)_2S{\cdot}BH_3 + 2BF_3$

A 7·8 c.c. sample of dimethylsulphide-boron trifluoride was prepared, and to this 3·3 c.c. of $B_2H_6$ was added. The mixture was equilibrated in a U-trap at −23° for one hour. The contents were then distilled from the −23° trap through a second trap at −140° into a third trap at −196°. The volume of the gas passing −140° was 5·8 c.c., which on hydrolysis yielded 3·4 c.c. of hydrogen; hence the 5·8 c.c. comprises 0·6 c.c. diborane and 5·2 c.c. boron trifluoride. The reaction proceeded, therefore, about 80 per cent to the right.

2. $2(CH_3)_3P{\cdot}BF_3 + B_2H_6 = 2(CH_3)_3P{\cdot}BH_3 + 2BF_3$

In a typical experiment, freshly sublimed trimethylphosphine-boron trifluoride (30·3 c.c.) was heated with diborane (10·6 c.c.) in a 500-ml bulb at 80° for 22 hours. After cooling to room temperature the bulb was frozen at −196° and attached to the vacuum line through a tube opener. The bulb was opened and it was observed that no substance was present with a finite vapour pressure at −196°. This indicated no hydrogen had been formed during the heating by the destruction of $BH_3$ groups. The bulb was warmed to room temperature and 20·1 c.c. of gas was recovered after passage through a trap at −78·5°; the latter was intended to condense any complex which sublimed during the recovery of more volatile materials.

The infra-red spectrum of the recovered gas was identical with that of pure boron trifluoride. When the gas was heated with water in a sealed tube, no hydrogen was formed, showing that diborane had not been present.

It may be concluded that the reaction proceeded quantitatively to the right, with displacement of boron trifluoride by diborane.

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3. $(CH_3)_3P{\cdot}BF_3 + (CH_3)_3N = (CH_3)_3N{\cdot}BF_3 + (CH_3)_3P$

A 32·2-c.c. sample of trimethylphosphine-boron trifluoride was heated with 32·0 c.c. of trimethylamine in a 500-ml bulb at 80° for 22 hours. After cooling to room temperature, the bulb was frozen at −196° and opened to the vacuum system. No hydrogen had been formed. The bulb was warmed to room temperature and 31·0 c.c. of gas was recovered after passage through a trap at −78·5°.

The infra-red spectrum of the recovered gas was identical with that of pure trimethylphosphine. The vapour pressure of the gas was 165·3 mm at 0°, and that expected for pure trimethylphosphine is 161 mm. Since the vapour pressure of trimethylamine at 0° is 680·5 mm, only a very small amount of this substance could be present. These results show that the reaction has proceeded quantitatively in favour of $(CH_3)_3N{\cdot}BF_3$ with displacement of trimethylphosphine by trimethylamine.

4. $2(CH_3)_3N{\cdot}BF_3 + B_2H_6 = 2(CH_3)_3N{\cdot}BH_3 + 2BF_3$

A 32·1-c.c. sample of trimethylamine-boron trifluoride was sealed up with 22·2 c.c. of $B_2H_6$ in a 500-ml bulb, which was heated for 12 hours at 80°. The only volatile products were 1·92 c.c. of hydrogen and 21·3 c.c. of unchanged diborane. The infra-red spectrum of the condensable gas showed no absorption in the 750-$cm^{-1}$ to 650-$cm^{-1}$ region, where boron trifluoride absorbs strongly. These results show that diborane does not displace boron trifluoride from trimethylamine under the conditions used.

5. $(CH_3)_3N{\cdot}BH_3 + (CH_3)_3P = (CH_3)_3P{\cdot}BH_3 + (CH_3)_3N$

A 28·2-c.c. sample of trimethylamine-borine was heated with 28·3 c.c. of trimethylphosphine in a 500-ml bulb at 120° for four days. The reaction bulb was cooled to room temperature and attached to the vacuum system where the volatile products were examined. No hydrogen was present, indicating that no pyrolysis of borine groups had occurred. The volume of the gas recovered, after passage through a trap at −78·5°, was 27·5 c.c. The weight of this gas was 76·6 mg, implying a molecular weight of 62·4; trimethylamine requires 59·1, trimethylphosphine 76·1.

The infra-red spectrum of the gas was consistent with a mixture of trimethylamine and trimethylphosphine, and from the molecular weight, the amounts of these gases are estimated as 22·2 c.c. and 5·3 c.c. respectively. These figures imply that the reaction has proceeded eighty per cent to the right. To put this important conclusion on a firmer basis, a method of analysis was devised for the mixture. This is based on the fact that trimethylphosphine reacts with carbon disulphide to form a nonvolatile substance, whereas trimethylamine does not react at all.[18] Application of the method to mixtures of trimethylamine and trimethylphosphine of known composition established its accuracy.

The 27·5-c.c. sample recovered from the above reaction was then treated with 83·3 c.c. of carbon disulphide in a trap so that a liquid phase was always present; this is important, as the reaction is rapid in the liquid phase but extremely slow in the gas phase.[18] The reaction is complete if no more red solid forms when the mixture is transferred to a clean trap. The volume of recovered gases, consisting of trimethylamine and excess of carbon disulphide, was 99·4 c.c. Treatment with 34.1 c.c. of boron trifluoride removed trimethylamine as its very stable complex, $(CH_3)_3N{\cdot}BF_3$. The remaining 12·2 c.c. of boron trifluoride was separated by distillation through a trap at −140°, where 77·6 c.c. of carbon disulphide were retained. These results show that the original mixture consisted of 21·9 c.c. of trimethylamine and 5·7 c.c. of trimethylphosphine, in good agreement with the composition expected from its molecular weight.

That the equilibrium was in favour of trimethylphosphine-borine and trimethylamine was confirmed by heating trimethylamine with $(CH_3)_3P{\cdot}BH_3$ when it was found that reaction 5 proceeded to the left to the extent of about 25 per cent.

## 3. DISCUSSION

By analogy with its behaviour towards trimethylaluminium and trimethylgallium, trimethylamine should form a more stable compound than trimethylphosphine with boron trifluoride. Available data confirm this expectation. Thus the compound trimethylamine-boron trifluoride shows no dissociation into its components at temperature as high as 177°.* Trimethylphosphine-boron trifluoride would be extensively dissociated at this temperature.[19] In agreement with these facts, we found that the displacement reaction:

$$(CH_3)_3P{\cdot}BF_3(s) + (CH_3)_3N(g) = (CH_3)_3N{\cdot}BF_3(s) + (CH_3)_3P(g)$$

went quantitatively to the right.

The adduct trimethylarsine-boron trifluoride does not appear to have been described but it is reasonable, in view of the existence of phosphine-boron trifluoride and the nonexistence of arsine-boron trifluoride,[20] to expect the stability order:

$$(CH_3)_3N{\cdot}BF_3 > (CH_3)_3P{\cdot}BF_3\ [> (CH_3)_3As{\cdot}BF_3],$$

where the brackets indicate a tentative but very reasonable conclusion.

Considering next the behaviour of Group-VI elements towards boron trifluoride, it was found by us that dimethylsulphide-boron trifluoride was more than 95 per cent dissociated into its components at room temperature and 65 mm pressure. The thoroughly characterized complex dimethylether-boron trifluoride is less than 20 per cent dissociated under similar conditions.[21] Dimethylselenide-boron trifluoride was found to be completely dissociated in the vapour phase. These observations indicate that the stability order of the complexes is:

$$(CH_3)_2O{\cdot}BF_3 > (CH_3)_2S{\cdot}BF_3 > (CH_3)_2Se{\cdot}BF_3.$$

It may be noted that volatility increases along this series, also indicative of decreasing stability, as mentioned in the Introduction. Thus the 0° saturation pressures of the complexes are 0·9 mm,[21] 45·5 mm, and 398 mm, respectively.

* It was earlier reported (A. B. BURG and A. A. GREEN *J. Amer. Chem. Soc.* **65**, 1838 (1943)) that trimethylamine-boron trifluoride was undissociated at 230°, but this result was later corrected (A. B. BURG and C. L. RANDOLPH, unpublished). The form of the tensimeter used in the earlier work was not suited for studies at higher temperatures, and errors arose in correcting for the vapour pressure of mercury (A. B. BURG, private communication).

[18] H. C. BROWN and R.H. HARRIS *ibid.* **71**, 2751 (1949).
[19] H. C. BROWN *J. Chem. Soc.* 1248 (1956).
[20] D. R. MARTIN and R. E. DIAL *J. Amer. Chem. Soc.* **72**, 852 (1950).
[21] H. C. BROWN and R. M. ADAMS *ibid.* **65**, 2557 (1943).

With trimethylborine as the reference acid, the order of co-ordination in Group V is:[17, 19, 22]

$$(CH_3)_3N{\cdot}B(CH_3)_3 > (CH_3)_3P{\cdot}B(CH_3)_3 > (CH_3)_3As{\cdot}B(CH_3)_3.$$

The work with trimethylborine reported here was carried out in order to determine and clarify the order of co-ordination with Group-VI elements as ligands.

It was expected that the complexes of trimethylborine with Group VI ligands would be very weak, since alkyl groups on boron reduce its acceptor power.[23, 10] This expectation was confirmed. It was found that dimethylether-trimethylborine was not formed at −78·5°, although dimethylsulphide and dimethylselenide both formed solid complexes at this temperature. In all three cases, dissociation was complete in the gas phase. Order of stability must therefore be inferred on the basis of saturation pressures, viz.:

$$(CH_3)_2S{\cdot}B(CH_3)_3 > (CH_3)_2Se{\cdot}B(CH_3)_3 > (CH_3)_2O{\cdot}B(CH_3)_3.$$

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It will be observed at once that this order is unusual. In analogy with boron trifluoride or trimethylaluminium, the expected order is O > S > Se, and even for trimethylgallium, the order is O > S. The unusual order can perhaps be understood in terms of two opposing effects: steric strain, brought about by interference between methyl groups on ligand and acceptor, which would be a maximum with dimethylether; and electron-pair donor power, which decreases with increasing size of the ligand. However, this is not necessarily the correct explanation for the anomalous order of co-ordination to trimethylborine. It may well be the result of those factors which may operate with borine itself, to be discussed below.

Orders of co-ordination with borine may now be compared. It was shown in the experimental part that dimethylsulphide-borine, which is only about 75 per cent dissociated in the gas phase at room temperature, is more stable than the dimethylselenide or dimethylether[24] complexes of diborane, both of which are completely dissociated in the gas phase. Thus, the order of co-ordination is:

$$(CH_3)_2S{\cdot}BH_3 > (CH_3)_2Se{\cdot}BH_3, \qquad (CH_3)_2O{\cdot}BH_3.$$

The relative order of the last two cannot be inferred from volatilities in this particular case. Although the selenium complex is less volatile, this may be due to its greater molecular weight. This is not a serious limitation, however, as the order S > O shows clearly enough that the order is anomalous when compared with boron trifluoride, trimethylaluminium, or trimethylgallium.

In passing, it may be mentioned that the new compounds described here with boron-selenium bonds imply the existence of a number of other boron-selenium compounds, which will probably have a similar relationship to the arsinoborines[28] as the thioborines[9] have to the phosphinoborines.[27]

It is interesting that towards both trimethylborine and borine the dimethyl compounds of the Group-VI elements have the same order of co-ordination, S > O. However, towards the alkyls of the Group-V elements, trimethylborine has the same order of co-ordination as trimethylaluminium and trimethylgallium. Although

[22] See also results of H. C. Brown discussed by J. Chatt *J. Chem. Soc.* 652 (1951).
[23] H. I. Schlesinger, N. W. Flodin, and A. B. Burg *J. Amer. Chem. Soc.* **61**, 1078 (1939).
[24] H. I. Schlesinger, and A. B. Burg *ibid.* **60**, 290 (1938); *Chem. Rev.* **31**, 1 (1942).

$(CH_3)_3N{\cdot}B(CH_3)_3$ ($\Delta H° = 17{\cdot}6$ kcal mole$^{-1}$)[17] is only slightly more stable than $(CH_3)_3P{\cdot}B(CH_3)_3$ ($\Delta H° = 16{\cdot}5$ kcal mole$^{-1}$),[19] the work of BROWN and his co-workers[19, 25] has shown that the compound trimethylamine-trimethylborine is weakened appreciably by steric strain. The P-B bond is longer than the N-B bond so steric effects in $(CH_3)_3P{\cdot}B(CH_3)_3$ would be less than in $(CH_3)_3N{\cdot}B(CH_3)_3$.[25] Thus in the absence of steric factors $(CH_3)_3N{\cdot}B(CH_3)_3$ would in all probability be appreciably more stable than $(CH_3)_3P{\cdot}B(CH_3)_3$. This would be in agreement with expectations of normal (donor) $\sigma$-bonding. However, the rather similar stabilities of $(CH_3)_3N{\cdot}B(CH_3)_3$ and $(CH_3)_3P{\cdot}B(CH_3)_3$ may not be entirely due to steric factors.

The complexes formed by treating trimethyl compounds of most of the Group-V elements with diborane have been characterized by BURG *et al.*[26, 27, 28] The compounds trimethylamine-borine and trimethylphosphine-borine are exceedingly stable, essentially undissociated in the vapour at 200°. The compound trimethylarsine-borine must dissociate near 100°, since if heated at this temperature the pyrolysis products of diborane are quickly formed.[28] The order of bonding in Group V towards the reference acid borine is thus N, P > As, but because of the high stabilities of both trimethylamine-borine and trimethylphosphine-borine, it was not clear until this investigation whether the order of co-ordination was one paralleling that found for all other Group-III acceptor molecules so far investigated, namely N > P > As or a new, hitherto unobserved order P > N > As.

The matter was resolved when it was shown that equilibrium in the reaction:

$$(CH_3)_3N{\cdot}BH_3(s) + (CH_3)_3P(g) = (CH_3)_3P{\cdot}BH_3(s) + (CH_3)_3N(g)$$

was about 80 per cent in favour of the products. Thus it may be concluded that:

$$(CH_3)_3P{\cdot}BH_3 > (CH_3)_3N{\cdot}BH_3 > (CH_3)_3As{\cdot}BH_3.$$

The anomalous orders of co-ordination to borine seem incapable of explanation on steric grounds. Steric effects in boron complexes should be more pronounced in the boron trifluoride series because of the larger size of the boron-trifluoride group,[29] and even more marked in the trimethylborine series. Yet the "normal" order of co-ordination is observed towards both boron trifluoride and trimethylborine in Group V, and in Group VI the expected order of co-ordination is found for boron trifluoride.

Attention may now be directed to a comparison of the relative strengths of complexes of borine and boron trifluoride. This is complicated by the dimerization of borine, a highly exothermic process which promotes the dissociation of borine complexes. An exact knowledge of the enthalpy change in the reaction:

$$B_2H_6(g) = 2BH_3(g)$$

would allow a quantitative comparison to be made, and for this reason the diborane-borine equilibrium assumes considerable importance. The first estimate of the energy required for the dissociation of one mole of diborane was apparently made by BELL and LONGUET-HIGGINS[30] who concluded that it involved absorption of at

[25] H. C. BROWN *Record Chem. Progress* (Kresge-Hooker Sci. Lib.) **14**, 83, (1953).
[26] A. B. BURG and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **59**, 780 (1937).
[27] A. B. BURG and R. I. WAGNER *ibid.* **75**, 3872 (1953).
[28] F. G. A. STONE and A. B. BURG *ibid.* **76**, 386 (1954).
[29] H. C. BROWN and R. H. HOROWITZ *ibid.* **77**, 1733 (1955).
[30] R. P. BELL and H. C. LONGUET-HIGGINS *Proc. Roy. Soc.* **A183**, 357 (1945).

least 15 kcal. The diborane-borine equilibrium has recently received attention from BAUER and his co-workers[31] who obtained the value $\Delta H^\circ = 28$ kcal mole$^{-1}$ by making a number of assumptions in the analysis of thermal and kinetic data.

It was found experimentally by MCCOY[31, 32]* that for the reaction:

$$(CH_3)_3N(g) + 1/2B_2H_6(g) = (CH_3)_3N{\cdot}BH_3(g)$$

$\Delta H^\circ = -17{\cdot}3$ kcal mole$^{-1}$. This may be combined with $\Delta H^\circ$ for the diborane-borine equilibrium to obtain:

$$(CH_3)_3N{\cdot}BH_3(g) = (CH_3)_3N(g) + BH_3(g)$$

with $\Delta H^\circ = 31{\cdot}3$ kcal mole$^{-1}$. This value is to be compared with that for the dissociation:

$$(CH_3)_3N{\cdot}BF_3(g) = (CH_3)_3N(g) + BF_3(g)$$

for which $\Delta H^\circ$ has been *estimated* as 26·6 kcal mole$^{-1}$. These values have led[31]* to the conclusion that when trimethylamine in the reference base, boron trifluoride appears to be a weaker acid than borine by about 5 kcal.

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It appears from more recent data that trimethylamine-boron trifluoride is more stable than this estimate implies. Thus LAWTON[33] has studied calorimetrically, in nitrobenzene, the reaction:

$$(CH_3)_3N(soln) + (CH_2)_5O{\cdot}BF_3(soln) = (CH_3)_3N{\cdot}BF_3(soln) + (CH_2)_5O(soln)$$

for which he found $\Delta H^\circ = -18{\cdot}09$ kcal mole$^{-1}$. If this equation is now combined with the equation:

$$(CH_2)_5O(soln) + BF_3(soln) = (CH_2)_5O{\cdot}BF_3(soln)$$

also in nitrobenzene, for which $\Delta H^\circ = -12{\cdot}8$ kcal mole$^{-1}$,[2] the enthalpy change in the dissociation:

$$(CH_3)_3N{\cdot}BF_3(soln) = (CH_3)_3N(soln) + BF_3(soln)$$

may be evaluated as 30·9 kcal mole$^{-1}$.

If it is true, as preliminary results of BROWN[2] seem to indicate, that the heats of formation of molecular addition compounds do not differ greatly in nitrobenzene solution and in the gas phase, it may be inferred that $\Delta H^\circ$ for the gas-phase dissociation of trimethylamine-boron trifluoride is close to 30·9 kcal mole$^{-1}$ as well. Comparison with the bond strength of 31·3 kcal mole$^{-1}$ in trimethylamine-borine leads to the conclusion that there is little difference in the strength of attachment to trimethylamine. Indeed in the absence of steric effects, it is possible that boron trifluoride would be

[31] A. SHEPP and S. H. BAUER *J. Amer. Chem. Soc.* **76**, 265 (1954).
[32] S. H. BAUER, A. SHEPP, and R. E. MCCOY *ibid.* **75**, 1003 (1953).
[33] E. A. LAWTON, Ph.D. Thesis, Purdue University, 1952.

* Since our paper was accepted for publication another paper by MCCOY and BAUER, *J. Amer. Chem. Soc.* **78**, 2061 (1956), has appeared. This paper describes the experimental work leading to the determination of $\Delta H^\circ = 31{\cdot}3$ kcal mole$^{-1}$ for the amine-adduct $(CH_3)_3N{\cdot}BH_3$. Furthermore, the dissociation energy of diborane is now given as $28{\cdot}5 \pm 2$ kcal mole$^{-1}$. Originally a value of 32 kcal mole$^{-1}$ was reported [32] but see reference 31, and the list of revised thermodynamic data appended to the new paper (*idem., loc. cit.*)

revealed as the stronger acid towards trimethylamine. However, the relative acid strength of borine and boron trifluoride is not always the same, but is very dependent on the ligand. Thus it was shown that the displacement reaction:

$$(CH_3)_3P{\cdot}BF_3(s) + 1/2B_2H_3(g) = (CH_3)_3P{\cdot}BH_3(s) + BF_3(g)$$

proceeded quantitatively to the right. Borine is thus more strongly bound than boron trifluoride to trimethylphosphine. Yet when $(CH_3)_3N{\cdot}BF_3$ was heated with diborane, using similar conditions, it was not possible to displace boron trifluoride. This indicates a greater stability difference in favour of the $BH_3$ adduct between $(CH_3)_3P{\cdot}BH_2$ and $(CH_3)_3P{\cdot}BF_3$ than between $(CH_3)_3N{\cdot}BH_3$ and $(CH_3)_3N{\cdot}BF_3$.

A rather similar variation of the order of acid strengths occurs in Group VI when oxygen and sulphur are the ligands. In the gas phase at ordinary temperatures, no interaction between dimethylether and diborane can be detected,[24] while the heat of dissociation of gaseous dimethylether-boron trifluoride is 13·3 kcal mole$^{-1}$.[21] Dimethylsulphide-borine, on the other hand, was sufficiently stable for us to evaluate $\Delta H^\circ$ for the reaction:

$$(CH_3)_2S{\cdot}BH_3(g) = (CH_3)_2S(g) + 1/2B_2H_6(g)$$

as 5·2 kcal mole$^{-1}$, and $\Delta S^\circ$ as 14·6 entropy units. Again we may utilize BAUER's[31, 32] estimates for the diborane-borine equilibrium to obtain for the reaction:

$$(CH_3)_2S{\cdot}BH_3(g) = (CH_3)_2S(g) + BH_3(g)$$

the values $\Delta H^\circ = 19{\cdot}2$ kcal mole$^{-1}$ and $\Delta S^\circ = 31{\cdot}7$ entropy units. This entropy increment is in reasonable agreement with the value 32·3 found[21] for the reaction:

$$(CH_3)_2O{\cdot}BF_3(g) = (CH_3)_2O(g) + BH_3(g).$$

This agreement in the $\Delta S^\circ$ values for the gas-phase dissociation of $(CH_3)_2S{\cdot}BH_3$ and $(CH_3)_2O{\cdot}BF_3$ supports the calculated $\Delta S^\circ$ for the dissociation of diborane.[31]

It might be expected that dimethylsulphide-boron trifluoride would be even more stable than dimethylsulphide-borine, in analogy with the stabilities observed towards dimethylether. To the contrary, the stability of dimethylsulphide-boron trifluoride was found to be so low that it was not possible to determine $\Delta H^\circ$ for its dissociation; at room temperature and 65 mm pressure, dissociation was more than 95 per cent complete. This fact indicates the much weaker character of boron trifluoride as an acid when dimethylsulphide is the ligand, and confirmation was further supplied when it was shown that the displacement reaction:

$$(CH_3)_2S{\cdot}BF_3(l) + 1/2B_2H_6(g) = (CH_3)_2S{\cdot}BH_3(l) + BF_3(g)$$

went about 80 per cent to the right.

Some results of H. C. BROWN[19] using pyridine (=Py) as the ligand are of interest in this discussion as well. If the rather large assumption is now made that the heat of dissociation of diborane is the same in nitrobenzene solution as in the gas phase, the following equations may be derived using BROWN's[19] results, again assuming the correctness of the enthalpy change for the diborane-borine equilibrium:[31, 32]

$$Py(soln) + BH_3(soln) = Py{\cdot}BH_3(soln) \qquad \Delta H^\circ = -31{\cdot}9 \text{ kcal}$$

$$Py(soln) + BF_3(soln) = Py{\cdot}BF_3(soln) \qquad \Delta H^\circ = -25{\cdot}0 \text{ kcal.}^{(2)}$$

Thus, when pyridine is the reference base, it appears that borine exceeds boron trifluoride in bonding power.

It is probably premature to arrive at a definite conclusion as to the exact acid strengths of $BF_3$ and $BH_3$ towards trimethylamine or dimethylether until more work is done. The data available so far indicate that acid strengths of $BH_3$ and $BF_3$ towards these ligands are rather similar. However it is clear from the work described here that borine bonds dimethylsulphide and trimethylphosphine better than does boron trifluoride.

It is convenient to summarize very briefly at this stage orders of co-ordination obtained here and elsewhere.[4, 6, 19]

(1) $(CH_3)_3N > (CH_3)_3P > (CH_3)_3As$ towards $BF_3$, $B(CH_3)_3$, $Al(CH_3)_3$, and $Ga(CH_3)_3$

$(CH_3)_3P > (CH_3)_3N \gg (CH_3)_3As$ towards $BH_3$

(2) $(CH_3)_2O > (CH_3)_2S$ towards $BF_3$, $Al(CH_3)_3$, and $Ga(CH_3)_3$

$(CH_3)_2S > (CH_3)_2O$ towards $BH_3$ and $B(CH_3)_3$

(3) $BH_3 > BF_3 > B(CH_3)_3$ towards $(CH_3)_3P$

$BH_3 > BF_3 > B(CH_3)_3$ towards $(CH_3)_2S$

$BH_3 > BF_3$ towards $(CH_3)_2Se$

$BF_3 > B_2H_6 > B(CH_3)_3$ towards $(CH_3)_2O$

The observed orders of stability $(CH_3)_3P{\cdot}BH_3 > (CH_3)_3P{\cdot}BF_3$ and $(CH_3)_2S{\cdot}BH_3 > (CH_3)_2S{\cdot}BF_3$, as well as the existence of $OC{\cdot}BH_3$ and $F_3P{\cdot}BH_3$[34] and the nonexistence of $OC{\cdot}BF_3$ and $F_3P{\cdot}BF_3$, are unexpected in terms of electronegativity predictions. Attachment of electronegative groups to an acceptor atom often results in an increase of dative-bond strength. Thus the heats of dissociation of the following compounds decrease in the order $(CH_3)_3N{\cdot}BF_3 > (CH_3)_3N{\cdot}B(CH_3)F_2 > (CH_3)_3N{\cdot}B(CH_3)_2F > (CH_3)_3N{\cdot}B(CH_3)_3$.[35] An increase in dative bond strength by substituting a more electronegative group on an acceptor atom is often offset, however, by other factors such as a change in the degree of availability of the vacant orbital on the acceptor atom, or perhaps the elimination of $\pi$-bonding which had been supplementing the simple dative $\sigma$-bond.

It is perhaps possible to account for the existence of $OC{\cdot}BH_3$ and $F_3P{\cdot}BH_3$ and the nonexistence of their boron trifluoride analogues by asserting that the bonding is classical in nature and that borine is merely a more powerful electron-pair acceptor. It is certainly true that the acceptor power of boron trifluoride has in the past been overrated.[36, 11]* Nevertheless it is rather unusual that when boron trifluoride and

[34] R. W. Parry and T. C. Bissot *J. Amer. Chem. Soc.* **78**, 1524 (1956).
[35] A. B. Burg and A. A. Green *ibid.* **65**, 1838 (1943).
[36] R. R. Holmes and H. C. Brown Abstracts of papers presented at the 129th meeting of the American Chemical Society, p. 28Q (1956).

* Since our paper was accepted for publication in this journal, H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.* **78**, 2173 (1956), have determined the relative acid strengths of the boron trihalides, towards pyridine, as $BF_3 < BCl_3 < BBr_3$. This order is contrary to electronegativity expectations, but the weakness of $BF_3$ as an acid is interpreted (*idem., loc. cit.*) in terms of X — B $\pi$-bonding increasing along the series $BBr_3$, $BCl_3$, $BF_3$, thereby reducing the acceptor power of boron. Such an effect could also account for $BF_3$ having a rather similar acid strength to $BH_3$ towards $(CH_3)_3N$, but it does not explain the unusual orders of co-ordination shown by ligands of Groups V and VI towards $BH_3$ or the much greater stability of $BH_3$ adducts over their $BF_3$ adducts when the ligand has vacant orbitals. Furthermore, although pyridine is a base of low steric requirements, the presence of its $\pi$-orbitals might lead to complications in the N—B bond, the effect changing with different groups on boron.

borine form complexes with ligands that can only bond by means of a classical $\sigma$-dative bond the stabilities of their adducts are rather similar; yet with ligands possessing vacant orbitals of low energy, such as dimethylsulphide or trimethylphosphine, the stability of the borine complexes is greatly enhanced over their boron trifluoride analogues. Moreover, borine shows an unusual order of co-ordination towards the donor atoms of Groups V and VI, an order of co-ordination not shown by any other Group-III acceptor molecule so far investigated, except trimethylborine which parallels borine in Group VI. With borine, as for the sub-group elements investigated such as platinum,[37] sulphur is a better donor than oxygen and phosphorus better than nitrogen.

The unusual co-ordination chemistry of borine is difficult to understand in terms of a steric effect, since the steric requirement of boron trifluoride is larger than borine, yet boron trifluoride preserves orders of co-ordination towards the ligand atoms of both Group V and VI expected for classical dative bonding. Perhaps the behaviour of borine can be understood by extending a suggestion made by BURG *et al.*[27, 28] to account for the unusual stability of certain phosphino- and arsino-borine polymers. Namely, that there may be a transfer of electron-density from B—H bonds to atoms bonded to boron having suitable vacant orbitals. Such behaviour may be of much more general occurrence in borine chemistry as a whole.

Indeed, it may be possible to treat the borine group in a borine complex like the methyl[38] group in organic chemistry, regarding the three hydrogen atoms as a *pseudo*-atom giving rise to a $\pi$-type orbital able to overlap empty orbitals, probably hybridized, provided by a suitable ligand atom. There might thus be a kind of $d_\pi$—$p_\pi$ bond in molecules like dimethylsulphide-borine, supplementing the classical dative $\sigma$-bond.

There is, however, an important difference between the effects postulated here and the "hyperconjugation" of organic chemistry. A charge separation occurs in a co-ordination compound like $(CH_3)_2\overset{+}{S}—\overset{-}{B}H_3$, which is very likely of a magnitude not usually encountered in organic chemistry. The drift of electron density from the borine group would lower the energy of the molecule not only by delocalization effects, but also by partial neutralization of the charge separation set up by the lone-pair $\sigma$-bond.

It is necessary to postulate that a similar drift of electron-density does not occur from the $BF_3$ group, or that if it does occur is of too small a magnitude to influence chemical behaviour. This postulate is reasonable when the high electronegativity of fluorine is considered. Moreover, WALSH[39] considers that the weakness of the boron-hydrogen bond renders it unique in some ways, arguing that the electron-cloud representing the bond is unusually diffuse.

A problem of long standing in the chemistry of the borine group is the existence of borine carbonyl.[40] A similar argument involving weak supplementary $\pi$-bonding with partial electron transfer from the B—H bonds to the vacant $2p_\pi$ orbital of carbon may account for the existence of $OC{\cdot}BH_3$,[41] and the apparent nonexistence of

[37] J. CHATT *et al.* *J. Chem. Soc.* 652 (1951); 2787, 4461 (1955).
[38] C. A. COULSON *Quart. Rev.* **1**, 144 (1947).
[39] A. D. WALSH in *Victor Henri Memorial Volume, Contribution to the Study of Molecular Structure.* DeSoer, Liege (1947) pp. 191–199.
[40] A. B. BURG and H. I. SCHLESINGER *J. Amer. Chem. Soc.* **59**, 780 (1937).
[41] A. B. BURG *Record Chem. Progress* (Kresge-Hooker Sci. Lib.) **15**, 159 (1954).

$OC{\cdot}BF_3$. Borine carbonyl has a low dipole moment and an HBH angle near 114°,[42] larger than that expected for tetrahedral boron, so the bonding may be somewhat like the multiple bonding in nickel carbonyl with the same effect on volatility.

There has been some difference of opinion as to the correct single-bond radius of the boron atom which perhaps renders unsatisfactory the deduction of the order of the boron-carbon bond from the observed bond distance. It is an experimental fact, however, that the boron-carbon distance in borine carbonyl is 1·540 Å,[42] in agreement with the corresponding distance in trimethylborine.[43] MULLIKEN[44] considers that the latter molecule is strongly stabilized by hyperconjugation. It may not be correct to assume that borine carbonyl is adequately described in terms of a $C \rightarrow B$ classical dative bond so weak that it fails to pull the boron atom very far out of the planar $sp^2$-arrangement.

Similarly, the recently discovered $F_3P{\cdot}BH_3$[34] may owe its existence to supplementary $\pi$-bonding involving overlap of the vacant 3*d*-orbitals of phosphorus and the *pseudo* $\pi$-orbital provided by the hydrogen atoms on boron. It is significant that phosphorus trifluoride does not bond other Group-III acceptor molecules, like boron trifluoride, yet it does form complexes with some of the subgroup elements, e.g., $Ni(PF_3)_4$,[45] where the bonding is believed to be multiple in character. It is true that the bonds in $OC{\cdot}BH_3$ and $F_3P{\cdot}BH_3$ are weak, but it should not be concluded that these molecules are adequately described in terms of the classical co-ordinate link on this account. It is significant that $NF_3$ does not add to the $BH_3$ group.[34] This is to be expected if the ideas presented here are correct. Although nitrogen is a superior electron-pair donor to phosphorus, the adduct $F_3N{\cdot}BH_3$ might not exist because nitrogen has no orbitals above the $2sp^3$-octet suitable for chemical bonding. No supplementary $\pi$-bonding is possible, and the only bonding mechanism is a classical $N \rightarrow B$ dative bond weakened by the electronegative fluorine atoms. In $F_3P{\cdot}BH_3$, the $\sigma$-dative bond is also weakened by the fluorine on phosphorus, but dative $\pi$-bonding is now possible and indeed enhanced by the fluorine atoms.

In conclusion, it seems appropriate to quote from MULLIKEN:[46]

"However, it must be kept in mind that the strength of a (Lewis) acid is not quite a unique absolute quantity, but depends appreciably on specific features of its interaction with the base with which it is paired."

*Acknowledgement*—It is a pleasure to acknowledge the generous support of this work by the United States Office of Naval Research.

[42] W. GORDY, H. RING, and A. B. BURG *Phys. Rev.* **78**, 512 (1950).
[43] H. A. LEVI and L. O. BROCKWAY *J. Amer. Chem. Soc.* **59**, 2085 (1937).
[44] R. S. MULLIKEN *Chem. Rev.* **41**, 207 (1947).
[45] G. WILKINSON *J. Amer. Chem. Soc.* **73**, 5501 (1951).
[46] R. S. MULLIKEN *ibid.* **74**, 811 (1952).



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# ON THE DICHROISM OF CERTAIN Co(III) COMPLEXES

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**Abstract**—Recent observations on the dichroism of certain diamagnetic cobaltic complexes are interpreted in terms of crystal field theory. Detailed agreement is obtained between theory and experiment, by recognizing the nature of the relevant transitions as electronically forbidden.

## INTRODUCTION

IN this note, we shall discuss the recent dichroic studies[1] by YAMADA, NAKAHARA, SHIMURA and TSUCHIDA of crystals containing the complex *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2Br_2]^+$ ions. We shall show that the crystal field theory,[2] which has had such striking successes in the last few years, is able to explain the measurements in detail. Our analysis is particularly concerned with the mechanism by which these electronically forbidden transitions acquire intensity.

In order to avoid duplication, we may confine our attention to the perchlorate of the dichloro complex. This crystallizes in the monoclinic system and has a well defined (001) plane, which is markedly dichroic. When viewed with light whose electric vector contains the *a* axis, the crystal appears blue; along the *b* axis it is a greenish yellow. The Cl-Co-Cl axis is nearly coincident with the *a* axis. More specifically, light is absorbed by a prominent band system near 6200 Å if the electric vector is along the *a* axis, but the crystal is then essentially transparent near 4300 Å. For the other, *b* direction of polarization, the absorption is weaker but still appreciable near 6200 Å, and quite strong at shorter wavelengths, showing a maximum at 4300 Å. Thus the 6200-Å band appears for light polarized parallel and perpendicularly to the Cl-Co-Cl axis, whereas the 4300 Å band is perpendicularly polarized only.

Although the actual symmetry of the complex ions cannot be higher than $D_{2h}$, other work on the spectra of ammines and ethylene diamine complexes shows that the effective symmetry is $D_{4h}$: spectroscopically, at least, *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(NH_3)_4Cl_2]^+$ are almost indistinguishable.[3] We shall therefore proceed as if we were dealing with the tetrammine. When the electric vector is parallel to the fourfold axis, it transforms like $A_{2u}$ of $D_{4h}$; when it is perpendicularly polarized, it transforms like $E_u$.

## CRYSTAL FIELD THEORY

The spectra of diamagnetic cobaltic complexes may be described, to good approximation, by the strong field limit, in which it is assumed that the stereospecific crystal forces prescribe the electronic motions, rather than their mutual repulsions. The six 3*d* electrons of the central ion are assigned to particular, largely atomic orbitals. In cases of octahedral symmetry, like those encountered in the hexammines, these orbitals are the stable, triply-degenerate $t_{2g}$ levels and the doubly-degenerate

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$e_g$ levels. The ground state of an octahedral complex is then $(t_{2g})^6$, a closed shell configuration of overall symmetry $^1A_{1g}$. The excited states arise by promoting a single $t_{2g}$ electron to an excited $e_g$ orbital, giving rise to $^1T_{1g}$ and $^1T_{2g}$ upper states, both of which are triply degenerate. The correlative interaction between the electrons, whose role has been subordinated by the crystal forces, is responsible for the separation between these two levels. Explicitly (vide infra), it is found that $^1T_{1g}$ lies some $16(F_2 - 5F_4)$ lower than $^1T_{2g}$.[4,5]

The complex ion in which we are interested may be regarded as derived from an octahedral analogue, say the hexammine, by means of a tetragonal perturbation, namely the substitution of two *trans*-ammonias by chloride ions. On going to crystal fields of this lower symmetry, the degeneracy of the excited states is partially removed. $^1T_{1g}$ of $O_h$ becomes $^1A_{2g}$ and $^1E_g$ of $D_{4h}$, and $^1T_{2g}$ becomes $^1B_{2g}$ and $^1E_g$. The orbital degeneracy is also split, the three $t_{2g}$ orbitals becoming $b_{2g}$ and an $e_g$ pair, whereas the octahedral $e_g$ pair have symmetry $a_{1g}$ and $b_{1g}$ in the lower group. The orbital configurations of the $^1A_{2g}(T_{1g})$ and $^1B_{2g}(T_{2g})$ states are therefore easily prescribed:

$$^1A_{2g}\colon\ (e_g)^4(b_{2g})(b_{1g}),$$

$$^1B_{2g}\colon\ (e_g)^4(b_{2g})(a_{1g}),$$

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(The separation of the octahedral $^1T_{1g}$ and $^1T_{2g}$ states in the strong field limit is most easily assessed by noting that $^1A_{2g}$ arises only from the former and $^1B_{2g}$ only from the latter.) The corresponding description of the $^1E_g$ states depends upon whether the tetragonal perturbation, or the intraionic, electronic repulsions are the more important. In the former event, these two states may be described by the configurations

$$^1E_g^{(1)}\colon\ (e_g)^3(b_{2g})^2(a_{1g}),$$

$$^1E_g^{(2)}\colon\ (e_g)^3(b_{2g})^2(b_{1g}),$$

respectively. In the latter, linear combinations of these are more apposite, namely,

$$^1E_g(T_{1g}) = \tfrac{1}{2}[\sqrt{3}\,{}^1E_g^{(1)} + {}^1E_g^{(2)}],$$

$$^1E_g(T_{2g}) = \tfrac{1}{2}[{}^1E_g^{(1)} - \sqrt{3}\,{}^1E_g^{(2)}].$$

To begin with, we shall use this second prescription (the determination of whose coefficients is described later.)

Now, in crystal field theory, the potential in which the electrons move is expanded in terms of spherical harmonics. On going from $O_h$ to $D_{4h}$, two new terms in this series are simultaneously operative, one involving second-order harmonics and the other fourth-order harmonics ($Y_2^0$ and $Y_4^0$). The concomitant splitting parameters are proportional, respectively, to $Ds$, $Dt$, say. Thus it is easily shown that the orbital levels are

$$\epsilon(a_{1g}) = \epsilon_0 + 6Dq - 2Ds - 6Dt,$$

$$\epsilon(b_{1g}) = \epsilon_0 + 6Dq + 2Ds - Dt,$$

$$\epsilon(b_{2g}) = \epsilon_0 - 4Dq + 2Ds - Dt,$$

$$\epsilon(e_g) = \epsilon_0 - 4Dq - Ds + 4Dt,$$

$\epsilon_0$ being a constant and $Dq$ being the usual parameter determining the splitting in perfectly octahedral fields.[1] The tetragonal perturbation makes contributions $(+14Dt)$ to the $^1A_{2g}$ state and $(-4Ds + 9Dt)$ to the $^1B_{2g}$ states. To the $^1E_g^{(1)}$, $^1E_g^{(2)}$ configuration it adds energies $(-Ds + 4Dt)$, $(+3Ds + 9Dt)$ respectively. Now, the centre-of-gravity rule applies separately to the components of the $^1T_{1g}$ state and to those of the $^1T_{2g}$ state so far as the second-order harmonics are concerned: the $Ds$ term for $^1E_g(T_{1g})$ must vanish and that for $^1E_g(T_{2g})$ must be equal to $(+2Ds)$. Accordingly, the energies of these two states are $(+5\frac{1}{4}Dt)$, $(2Ds + 7\frac{3}{4}Dt)$ respectively, and the coefficients listed earlier are obtained for a suitable choice of phase factors. The tetragonal splitting of the excited octahedral states are

$$E[^1A_{2g}(T_{1g})] - E[^1E_g(T_{1g})] = 8\tfrac{3}{4}Dt,$$

$$E[^1E_g(T_{2g})] - E[^1B_{2g}(T_{2g})] = 6Ds - 1\tfrac{1}{4}Dt.$$

The signs and relative magnitudes of $Ds$, $Dt$ naturally depend upon the nature of the tetragonal distortion undergone by the octahedron.

From their location in the spectrochemical series, we should expect the perturbation describing the replacement of two $NH_3$ ligands by $Cl^-$ to have the sense of attracting the electrons of the ion into the regions lying on either side of the central ion, on the four-fold axis. The localized fourth-order harmonics describe this most specifically and we therefore set $Dt > 0$ (for in this way, the $a_{1g}$ orbital, which is also directed along this axis, is particularly stabilized). Therefore, the splitting of the lowest group of octahedral states is predicted to be in the sense that $^1E_g(T_{1g})$ is lowered with respect to $^1A_{2g}(T_{1g})$. The former is likely to be yet further depressed by configurational interaction with $^1E_g(T_{2g})$, under the influence of the tetragonal distortion.

Assuming that both the 6200 Å and the 4300 Å systems in the *trans*-$[Co(en)_2Cl_2]^+$ complex ion arise from a splitting of the first excited octahedral state, namely $^1T_{1g}$, we should on this basis make the respective assignments $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$.[8] Our assumption that the $^1T_{2g}$ levels lie at shorter wave lengths receives some empirical support, based on comparisons of the spectra of octahedral complexes and those of lower symmetry.[3]

## ANALYSIS

We shall now attempt to make an assignment of the observed bands, based on selection rules. Though the temperature at which the spectra were measured is not stated,[1] we shall suppose the main part of the absorption to occur from a vibrationally unexcited ground state. The low intensity of the bands confirms that they are electronically forbidden and presumably $g \rightarrow g$. We shall therefore attribute the intensity to vibrational perturbations in making our analysis.[9]

An upper $^1A_{2g}$ state can only appear in absorption with the simultaneous excitation either of an $\alpha_{1u}$ ($a$-axis polarization) or of an $\epsilon_u$ ($b$-axis) vibrational mode. For an upper $^1B_{2g}$ state, these vibrational motions have symmetry $\beta_{1u}$ or $\epsilon_u$ respectively. Transitions to an upper $^1E_g$ state, however, are allowed by $\epsilon_u$ ($a$ axis) or by $\alpha_{1u}$, $\alpha_{2u}$, $\beta_{1u}$ or $\beta_{2u}$ ($b$ axis) excitations.

Now, treating the $Cl^-$ and $NH_3$ or ethylene diamine ligands as if these were point masses in a complex like *trans*-$[CoX_4Y_2]$, it is easy to see that although there are stretching modes of symmetry $\alpha_{2u}$ and $\epsilon_u$, there are no stretching or bending modes of symmetry $\alpha_{1u}$ or $\beta_{1u}$. That the 6200-Å system is seen for both parallel and perpendicular

polarizations strongly suggests that this is indeed the predicted $^1A_{1g} \rightarrow {}^1E_g$ transition. On the other hand, since the 4300-Å system is seen for b-axis polarization alone, this must be attributed to the absence of "enabling" vibrations of symmetry $\alpha_{1u}$ or $\beta_{1u}$, depending on whether the upper state has symmetry $^1A_{2g}$ or $^1B_{2g}$ respectively. If we accept the empirical correlation of the 4300-Å band with an upper component of the lowest octahedral group of states, its assignment is $^1A_{1g} \rightarrow {}^1A_{2g}$ as predicted. On the spectroscopic evidence concerning the $[Co(en)_2Cl_2]^+$ ion alone, however, this cannot be distinguished from the alternative assignment $^1A_{1g} \rightarrow {}^1B_{2g}$.

(1) S. YAMADA, A. NAKAHARA, Y. SHIMURA, and R. TSUCHIDA *Bull. Chem. Soc. (Japan)* **28**, 222 (1955).
(2) e.g., particularly, L. ORGEL *J. Chem. Soc.* 4756 (1952) *J. Chem. Phys.* **23**, 1004, 1819, 1824, 1958 (1955); or a recent review by W. MOFFITT and C. J. BALLHAUSEN *Annual Reviews of Physical Chemistry* Vol. 7 (1956).
(3) R. TSUCHIDA *J. Chem. Soc. (Japan)* **59**, 586 (1938); M. LINHARD and M. WEIGEL *Z. Anorg. Chem.* **271**, 101 (1953); F. BASOLO, C. J. BALLHAUSEN and J. BJERRUM *Acta Chem. Scand.* **9**, 810 (1955).
(4) e.g., E. U. CONDON and G. H. SHORTLEY *Theory of Atomic Spectra* Cambridge Univerity Press (1935).
(5) In ORGEL's 1952 paper,[2] this is given incorrectly as $12(F_2 - 5F_4)$ due to a slight error in one of his formulae.
(6) e.g., K. W. H. STEVENS *Proc. Phys. Soc. A* **65**, 209 (1952).
(7) R. SCHLAPP and W. G. PENNEY *Phys. Rev.* **42**, 666 (1932).
(8) This assignment was suggested by ORGEL in 1952[2] on the basis of an eigenfunction which is not correct and attributed to the *Ds* rather than the *Dt* term.
(9) e.g., G. HERZBERG and E. TELLER *Z. phys. Chem.* **197**, 239 (1931).

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# X-RAY MEASUREMENTS OF THE THERMAL EXPANSION OF TRIGONAL POTASSIUM, LITHIUM, AND SILVER NITRATES

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**Abstract**—The thermal expansion of the trigonal high-temperature modifications of $LiNO_3$, $KNO_3$ and $AgNO_3$ has been measured. Cell constants at the transition and melting points and expansion coefficients are tabulated for the three salts and for $NaNO_3$. The expansion of these crystals is strongly anisotropic, being greatest along the hexagonal *c*-axis. For $KNO_3$, the expansion perpendicular to this axis was found to be slightly negative.

## INTRODUCTION

THE nitrates of Li, Na, K, Rb, and Ag crystallize from the melt as trigonal, isostructural crystals. For $LiNO_3$, the trigonal modification is still stable at room temperature; the other nitrates have at least one polymorphic transition between the melting point and room temperature, leading to different modifications for the different salts. These transitions have been associated with the onset of rotation of the nitrate ions.[1] The present measurements were undertaken in order to determine the cell dimensions of the trigonal high-temperature forms at the transition points which were required for an analysis of the spatial possibility of group rotation in these crystals. A preliminary account of this analysis has already been given;[2] it was shown that the rotation of the nitrate ions is rather restricted by overlap with neighbouring atoms and that another mode of thermal motion, viz. linear vibration of the nitrate group perpendicular to its own plane, should be more important for the thermal behaviour of these crystals. The purpose of the present paper is to report the experimental information obtained; a full account of the spatial considerations will be given later.

## METHOD OF MEASUREMENT

The X-ray measurements were made with a one-sided Debye-Scherrer heating camera* of 4·55 cm film radius, using Cu*K* radiation. The temperature was controlled by a thermocouple in connection with a Hartmann and Braun temperature regulator and was known to within ±2·5°C. The thermocouple was repeatedly calibrated against known melting points.[3] The samples were mounted in pyrex capillaries of 0·3 mm diameter; to preclude thermal decomposition when the camera was evacuated, the capillaries were sealed at both ends. No chemical attack on the glass was observed. Commercial chemicals were used throughout (Baker's analysed, c.p. grade).

A somewhat detailed description of the X-ray technique may be appropriate since it was used also in similar measurements on the alkali sulphates. Owing to the rapid decrease of the intensity of back reflexion lines, the cell constants had often to be determined from forward reflexions. This required accurate correction for eccentricity and absorption in the sample. The following procedure

* Designed by Prof. G. HÄGG and constructed in the workshop of the Institute.

[1] F. C. KRACEK, T. F. W. BARTH and C. J. KSANDA *Phys. Rev.* **40**, 1034 (1932).
[2] H. F. FISCHMEISTER Lecture at Physics Conference, Stockholm, Sept. 1955; *Arkiv. Fysik* (in press)
[3] H. F. FISCHMEISTER *Acta Cryst.* **9**, 416 (1956).

was adopted. The camera is equipped with a movable film holder which allows six exposures to be made on one film. One of these was always taken at room temperature and a correction curve for the combined errors, valid for that particular run, was derived from it. The constancy of the eccentricity error with temperature had been checked previously during the course of measurements with NaCl.[8] Accurate values of the room temperature cell constants were obtained from powder photographs taken with Cu $K_\alpha$ radiation ($\lambda_\alpha^- = 1{\cdot}54179$ Å) in a GUINIER type focusing monochromator camera, using NaCl as an internal standard ($a_{NaCl} = 5{\cdot}63984$ Å). The theoretical line positions calculated from these cell constants were used in setting up the correction curves for the expansion films.

Prior to measurement, the expansion films were contact printed on glass plates, to avoid the irregular contraction of the cellulose base under the slight heating action of the measuring projector. Values of $\sin^2\theta$ were calculated from both $K_\alpha$ and $K_\beta$ lines and corrected as described above. Cell constants were then derived from each individual spectrum by means of a least-squares treatment. These constants were plotted against temperature, and the cell dimensions at the transition and melting point were obtained by extrapolation of these points. This was preferred to the simpler procedure of smoothing the primary ($\theta$ or $\sin^2\theta$ data), because the latter method involves the risk of falsifying the shape of the expansion curve and gives an incorrect impression of the experimental scatter.

To verify the physical appropriateness of the least-squares results, the differences $D_{hkl} = \sin^2\theta_{obs} - \sin^2\theta_{calc}$ were tabulated for each spectrum, and in a few cases lines for which this quantity exceeded ca. 0·0010 were omitted in another least-squares calculation. The justification of such rejections was also checked by plotting the primary data ($\sin^2\theta_{obs}$) against temperature. For the final cell constants, the average deviation

$$\overline{|D|} = \Sigma\,|\sin^2\theta_{obs} - \sin^2\theta_{calc}|/n$$

(where $n$ = number of measurable lines) ranged between $0{\cdot}0001_8$ and $0{\cdot}0005_1$. The most severe limitation of the certainty of the high-temperature cell constants is the paucity of safely measurable lines (the number of which was between seven and fourteen); next to this comes probably the uncertainty of temperature determination. The overall uncertainty of the results is estimated at ±1 part in a thousand. This accuracy is still fully sufficient for the discussion of the spatial aspects of group rotation.

## EXPERIMENTAL RESULTS

The results of the high-temperature measurements are summarized in Table 1, which contains the (extrapolated) dimensions of the hexagonal unit cell chosen for

TABLE 1.—CELL CONSTANTS OF THE TRIGONAL MONOVALENT NITRATES

| Salt | Temperature | Reference | Hexagonal | | Primitive rhombohedral | | Rhombohedral | | Coefficient of expansion† | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $t$, °C | | $a$, Å | $c$, Å* | $r$, Å | $\alpha$ | $r'$, Å | $\alpha'$ | $\lambda \mid a \times 10^6$ | $\lambda \mid c \times 10^6$ |
| $LiNO_3$ | 20°<br>251·4° | | 4·692<br>4·729 | 15·206<br>15·577 | 3·710<br>3·768 | 78° 27′<br>77° 44′ | 5·747<br>5·866 | 48° 11′<br>47° 33′ | +34 | +103 |
| $NaNO_3$ II<br>$NaNO_3$ I | 18°<br>275°<br>310° | (6), (7)<br>(4), (7)<br>(4) | 5·060<br>5·075<br>5·075 | 16·784<br>17·523<br>17·607 | 4·044<br>4·134<br>4·147 | 77° 27′<br>75° 40′<br>75° 27′ | 6·313<br>6·535<br>6·560 | 47° 15′<br>45° 42′<br>45° 31′ | 0 | +136 |
| $KNO_3$ I | 128°<br>335° | | 5·423<br>5·414 | 19·277<br>20·590 | 4·486<br>4·642 | 74° 22′<br>71° 21′ | 7·148<br>7·542 | 44° 35′<br>42° 04′ | −8 | +308 |
| $RbNO_3$ I | 250° | (5) | $5{\cdot}48_3$ | $21{\cdot}41_0$ | 4·77 | 70° 10′ | $7{\cdot}80_7$ | 41° 07′ | | |
| $AgNO_3$ I | 150·4°<br>210° | | (5·168)<br>(5·174) | (16·903)<br>(17·018) | (4·103)<br>(4·119) | (78° 04′)<br>(77° 48′) | (6·342)<br>(6·411) | (47° 49′)<br>(47° 36′) | +23 | +134 |

* $2c$ for $NaNO_3$ I, $KNO_3$ I, $RbNO_3$ I, $AgNO_3$ I.
† At melting point

the calculations at the transition and melting point. This cell contains twelve formula units and corresponds to the hexagonal unit of $LiNO_3$ and $NaNO_3$ II, the low-temperature form isomorphous with calcite. Owing to the disordering of the anions, the true hexagonal unit cell of some of the salts has half the $c$ axis of this cell. Table 1 also lists the extrapolated dimensions of the two alternative rhombohedral cells at the transition and melting point. The corresponding constants for $NaNO_3$ I—calculated from the interferometric measurements of AUSTIN and PIERCE[4] are given for comparison, as well as the cell constants of $RbNO_3$ I at 250°C which are known from the work of FINBANK, HASSEL, and STRØMME.[5]

*Potassium nitrate*

This salt was the main object of the present study. The cell constants of the orthorhombic room-temperature modification ($KNO_3$II) are

$$a = 5{\cdot}4175 \pm 0{\cdot}0010 \text{ Å};$$

$$b = 9{\cdot}1709 \pm 0{\cdot}0007 \text{ Å};$$

$$c = 6{\cdot}4255 \pm 0{\cdot}0008 \text{ Å};$$

They were determined from internal-standard Guinier films and from the high-precision data used by HESSE[8] in his study on the indexing of the powder patterns of orthorhombic crystals*). These data had been obtained with focusing cameras of the Hägg-Phragmén type. The two sets of results were in perfect agreement. The cell constants are in good accord with published values: EDWARDS[9] obtained $a = 5{\cdot}43$ Å, $b = 9{\cdot}17$ Å, $c = 6{\cdot}45$ Å. A further check is afforded by extrapolation of COHEN and BREDEÉ's accurate density measurements[10] (between 30 and 128°C) to room temperature, which gives $d_{18°C} = 2{\cdot}1068$ as against 2·1032 from the above cell constants.

The high-temperature measurements are presented in Fig. 1 which shows the dimensions of the hexagonal unit cell as a function of temperature. In Table 2 they are compared with published data.

TABLE 2.—COMPARISON OF PRESENT AND PREVIOUS RESULTS ON $KNO_3$ I

| Temperature | TAHVONEN[11] | Present work | COHEN and BREDEÉ[10] |
|---|---|---|---|
| 128°C | — | $d =$ 2·0513 | $d =$ 2·0337 |
| | $a =$ 5·396 Å | $a =$ 5·420 Å | |
| 152°C | $c =$ 19·410 Å | $c =$ 19·410 Å | |
| | $d =$ 2·0577 | $d =$ 2·0395 | $d =$ 2·0211 |

* The author is indebted to phil. mag. R. HESSE for permission to use his material, including unpublished backreflexion data.

[4] J. B. AUSTIN and R. H. H. PIERCE *J. Amer. Chem. Soc.* **55**, 661 (1933).
[5] CHR. FINBAK, O. HASSEL, and L. C. STRØMME *Z. phys. Chem.* **B37**, 468 (1937).
[8] J. WEIGLE *Helv. Phys. Acta* **7**, 46 (1934).
[7] H. SAÏNI and A. MERCIER *Helv. Phys. Acta* **7**, 267 (1934).
[8] R. HESSE *Acta Cryst.* **1**, 200 (1948).
[9] D. A. EDWARDS *Z. Kryst.* **A80**, 150 (1931).
[10] E. COHEN and H. L. BREDEÉ *Z. phys. Chem.* **A140**, 391 (1929).
[11] P. E. TAHVONEN *Ann. Acad. Sci. Fenn. Ser.* A I, Math-Phys. No. **44** (1947).

TAHVONEN used a Hägg-Phragmén camera, which should make his results less susceptible to accidental errors; yet his value of the density diverges twice as much from COHEN and BREDEÉ's as does the present author's. However, dilatometric density measurements above a transition point where fragmentation of the crystals and formation of internal flaws[12, 13] occurs must be regarded with caution. Although the absolute discrepancy between X-ray and dilatometric density is about three times the estimated uncertainty of the X-ray work (0·9% against 3 × 0·1%), its constancy—again within the limits of accuracy of these experiments—speaks for the correctness of the expansion data obtained.

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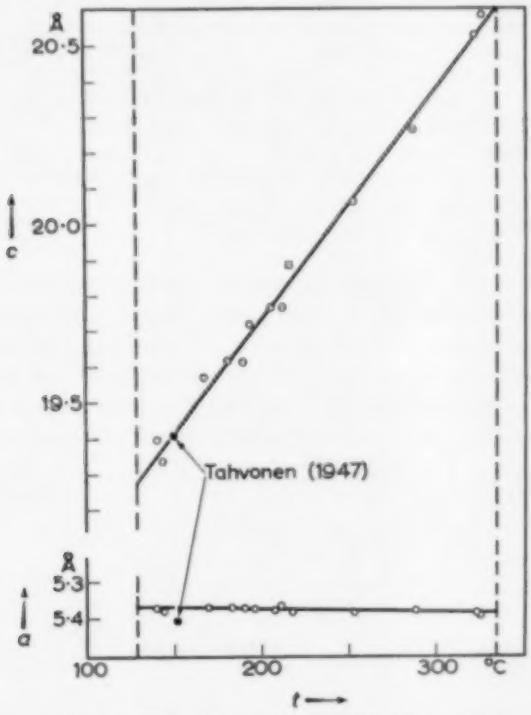


FIG. 1.—Thermal expansion of $KNO_3$ I (hexagonal axes).

Within experimental accuracy, the expansion of $KNO_3$ I is linear over the whole temperature range of its existence (as is that of the other salts investigated here). The predominant expansion along the *c* axis, i.e., perpendicular to the plane of the anions, is characteristic of all crystals of the calcite type so far investigated.[14] In the case of $KNO_3$ I, this is particularly emphasized, the expansion along the other axis being negtive. Although this contraction is too small in comparison with the experimental uncertainty to be considered as absolutely certain, it is not surprising when viewed in connection with the expansion coefficients of the whole group of trigonal alkali nitrates (cf. Table 1).

[12] S. W. KENNEDY, A. R. UBBELOHDE, and I. WOODWARD *Proc. Roy. Soc.* **A219**, 303 (1953).
[13] W. J. DAVIS, S. E. ROGERS, and A. R. UBBELOHDE *Proc. Roy. Soc.* **A220**, 14 (1953).
[14] J. J. LANDER *J. Chem. Phys.* **17**, 892 (1949).

### *Lithium nitrate*

Only eight high-temperature measurements were made on this salt; the high-temperature spectra confirmed the previously reported absence of a transition.[1] The cell constants at room temperature (from internal standard Guinier films) are given in Table 1; they are in good agreement with ZACHARIASEN's values,[15] $a = 4{\cdot}67$ Å, $c = 15{\cdot}19$ Å.

### *Silver nitrate*

Too great weight should not be attached to the cell constants given for this salt. The transition at 159·4°C involves excessive fragmentation so that satisfactory X-ray lines could only be obtained after prolonged recrystallization near the melting point. The heating times were further extended by the necessity of long X-ray exposures—the tube was run at 25 kVp to avoid Ag *K* fluorescence—so that considerable decomposition may have occurred. Although this will affect the absolute values of the cell constants, the expansion characteristics of a crystal are known to depend but little on its purity, so that the observed anisotropy of expansion should be fairly certain. One sample gave the trigonal spectrum even after cooling to room temperature, probably owing to heat and radiation damage. An internal standard Guinier photograph of this sample gave the cell constants: $a = 5{\cdot}161$ Å, $2c = 16{\cdot}621$ Å. No extra lines indicating a doubling of $c$ (i.e., ordering of the anions) in the undercoated state were found. After a week, the sample had transformed to the orthorhombic modification ordinarily stable at room temperature. No X-ray results have previously been reported for $AgNO_3$ I, but the existence of a trigonal modification has been recognized in optical work.[16]

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[15] W. H. ZACHARIASEN *Skrifter Norske Vidensk. Akad.* Oslo, No. 4 (1928).
[16] O. GROTH *Chemische Krystallographie*, Vol. II (Leipzig, 1906–19).

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# THIOIODIDE FORMATION BY PHOSPHORUS

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**Abstract**—The compounds PSI and $P_2SI_4$ cannot be prepared by the methods claimed in the literature, the usual reaction product being a mixture of tetraphosphorus trithiodi-iodide, $P_4S_3I_2$, tetraphosphorus heptasulphide and phosphorus iodides. $P_4S_3I_2$ may be obtained in high yield from the elements in correct proportions.

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AFTER work on the silicon thiochlorides,[1] an attempt was made to determine the interrelationships of the phosphorus thioiodides, $P_4S_3I_2$, PSI, and $P_2SI_4$ reported by OUVRARD.[2, 3] It was found, however, that only $P_4S_3I_2$ could be prepared.

The compound PSI has been claimed[3] to be formed from four reactions,[4] namely those between (*1*) yellow phosphorus, sulphur and iodine in equi-atomic proportions; (*2*) phosphorus tri-iodide and hydrogen sulphide; (*3*) phosphorus tri-iodide and the supposed phosphorus sulphide[5] "$P_2S_3$" and (*4*) iodine and "$P_2S_3$." Reaction (*1*) carried out in carbon disulphide is now found to yield tetraphosphorus trithiodi-iodide, $P_4S_3I_2$, phosphorus tri-iodide and red phosphorus, while at 125° tetraphosphorus heptasulphide is also formed. The heptasulphide and the same thioiodide are also obtained from reaction (*2*). In neither case is there evidence of any intermediate product even under very mild conditions of reaction. No reaction whatever occurs between phosphorus tri-iodide and a sulphide melt of composition $P_2S_3$ at the low temperature (<75°) implied by OUVRARD, or between "$P_2S_3$" and iodine in carbon disulphide. The existence of compounds PSI and $P_2SI_4$ (also claimed to be produced from "$P_2S_3$" and the tri-iodide) is thus open to serious doubt. OUVRARD mentions neither the precise conditions for their preparation nor any means of characterization.

The compound $P_4S_3I_2$ has itself been reported[2, 3] as formed from (*5*) hydrogen sulphide and diphosphorus tetraiodide at 110–120°; (*6*) combination of the elements in correct proportions; and (*7*) iodine and tetraphosphorus trisulphide.[6] Repetition of these experiments indicated that reaction (*5*) failed to yield tetraphosphorus trithiodi-iodide, that it is formed together with the heptasulphide and an iodide from (*7*), and that it may be obtained in almost quantitative yield from reaction (*6*). The compound (m.p. 120·5°) is orange-yellow, but becomes pale yellow at liquid air temperature. In moist air it smells of hydrogen sulphide, but it is not visibly changed. It is monomeric in carbon disulphide.

The formation of tetraphosphorus trithiodi-iodide in reaction (*7*) represents an intermediate stage of the iodination, since this compound itself is now found to react further with iodine to give phosphorus heptasulphide and phosphorus tri-iodide It is thus evident why WOLTER[6] who slowly added iodine to tetraphosphorus tri-

sulphide in equimolecular proportion obtained the thioiodide, while TREADWELL and BEELI[7] using excess iodine found the end products only. The formation of heptasulphide in reactions (*1*), (*2*), and (*7*) points to considerable bond mobility.

The structural relationship of tetraphosphorus trithiodi-iodide to the phosphorus sulphides[8] is of interest and Dr. B. R. PENFOLD is making an X-ray analysis of the compound in this laboratory.

## EXPERIMENTAL

Phosphorus tri-iodide (m.p. 60°) and diphosphorus tetraiodide (m.p. 124°) were obtained by combination of the elements in sulphur-free carbon disulphide[9] followed by recrystallization. Phosphorus sulphides were prepared by the method of STOCK.[10]

Reaction products were separated by fractional crystallisation from (purified) carbon disulphide cooled in low-temperature baths. Separation of intermediate fractions was carried sufficiently far to ensure that no constituents were overlooked. Purified samples were freed from residual solvent under vacuum at room temperature. All manipulations were made under dry carbon dioxide.

### *Reaction between Yellow Phosphorus, Sulphur, and Iodine*

(*A*) *In Equiatomic Proportions.* A solution of the elements (0·23 g atom of each) in carbon disulphide was allowed to stand for one hour and the solvent then removed during three hours on a water bath. The soluble product was dissolved from a little red phosphorus with carbon disulphide. Repeated fractional crystallization enabled identification of the trithiodi-iodide (m.p. 118°) and a smaller amount of the more soluble phosphorus tri-iodide. A little red solid also obtained (<0·5 g, m.p. 124° and of low solubility in carbon disulphide) was probably diphosphorus tetraiodide.

In a second experiment the temperature was raised to 125° after removal of the solvent. The insoluble residue was tetraphosphorus heptasulphide (m.p. 305°) but the extract again contained tri-iodide and trithiodi-iodide.

(*B*) *In the Ratio* $4P : 3S : 2I$. The elements (25 g total) were brought together in carbon disulphide, the solvent removed and the residue brought to fusion in an oil bath at 120–125° for one hour. (The reaction was found incomplete at 60°.) The product was extracted (residue <0·5 g) and the trithiodi-iodide recovered by cooling to −78°. After recrystallization (m.p. 120·5°) the composition found was: P, 25·9, 25·9; S, 20·3, 20·4; I, 53·2 per cent; M, ebullioscopic in carbon disulphide, 514, 523. ($P_4S_3I_2$ requires P, 26·2; S, 20·3; I, 53·5 per cent; M, 474.)

### *Reaction between Phosphorus Tri-iodide and Hydrogen Sulphide*

Dry hydrogen sulphide was passed over the molten iodide (25 g) in a glass trough, for 15 hours at 100°. Unchanged tri-iodide and a residue of heptasulphide (m.p. 303–304°) were obtained. A second reaction continued for only 9 hours at 100° gave the same products. A run at 112° for 8 hours yielded in addition a small amount of the trithiodi-iodide (m.p. 118–119°).

### *Reaction between Diphosphorus Tetraiodide and Hydrogen Sulphide*

The gas was passed over the iodide for 40 hours at 105–110°. Extraction of the product showed it to consist of red phosphorus and a mixture of phosphorus sulphides. The same products, together with unchanged tetraiodide, were obtained from a run discontinued before reaction was complete (16 hours).

### *Reaction of Iodine with Tetraphosphorus Trisulphide*

The iodine (5·1 g in 50 c.c. carbon disulphide) was added slowly to the sulphide (4·8 g in 20 c.c.). A little heptasulphide (m.p. 303°) crystallized on standing. The thioiodide (m.p. 108°) recovered from the solution by addition of ligroin, followed by cooling, proved difficult to purify. For preparative purposes the method is thus inferior to direct synthesis.

### *Analysis*

Sulphur and phosphorus were determined gravimetrically, the sample being absorbed in alkali (about 5N) and oxidized by addition of bromine.[11] For iodine the Carius method (at 170°) was used.

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## REFERENCES

[1] D. J. Panckhurst, C. J. Wilkins, and P. W. Craighead *J. Chem. Soc.* 3395 (1955).
[2] L. Ouvrard *Compt. Rend.* **115**, 1301 (1892).
[3] L. Ouvrard *Ann. Chim. Phys.* **7** (2), 221 (1894).
[4] E. Dreschel *J. Prakt. Chem.* **10** (2), 180 (1874), also suggested the formation of a compound PSI as an intermediate in the complex reaction between phosphonium iodide and carbon disulphide in a sealed tube above 140°.
[5] C. Beeli *Helv. Chim. Acta* **18**, 1172 (1935), reports that a slowly cooled melt of composition 2P : 3S can be separated into $P_4S_5$ and $P_4S_7$. See also ref. (7).
[6] L. Wolter *Chem. Ztg.* **31**, 640 (1907).
[7] W. D. Treadwell and C. Beeli *Helv. Chim. Acta.* **18**, 1161 (1935).
[8] (a) A. Vos and E. H. Wiebenga *Acta Cryst.* **8**, 217 (1955); (b) S. van Houten, A. Vos, and G. A. Wiegers *Rec. Trav. Chim.* **74**, 1167 (1955).
[9] F. E. E. Germann and R. N. Traxler *J. Amer. Chem. Soc.* **49**, 307 (1927).
[10] A. Stock and M. Rudolf *Ber.* **43**, 150 (1910).
[11] E. L. Baldeschwieler *Ind. Eng. Chem. (Anal. Edn.)* **6**, 402 (1934).

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# A STUDY OF THE CALCIUM REDUCTION OF BERYLLIUM OXIDE

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**Abstract**—The calcium reduction of beryllium oxide has been studied in some detail. It has been shown that the reaction takes place when the calcium melts, and yields a mixture of calcium oxide and of the compound $CaBe_{13}$. Provided that calcium is present in considerable excess the reduction goes substantially to completion. The compound $CaBe_{13}$ is readily separated from the lime and excess calcium by leaching in cold dilute acetic acid. Attempts to remove the calcium from the $CaBe_{13}$ by vacuum distillation and by reaction with hydrogen, magnesium, bismuth, or lead were not successful. This behaviour suggests that $CaBe_{13}$ is a moderately stable compound.

## INTRODUCTION

IN the course of a study of the reduction of certain metal oxides by calcium and magnesium the reaction between beryllium oxide and calcium was investigated. Beryllium oxide is thermodynamically one of the most stable metal oxides, the free energy change for the reaction

$$BeO + Ca \rightarrow Be + CaO$$

being only about 5 kcals/mole at moderate temperatures. A previous study of the calcium-beryllium oxide reaction is recorded in the literature. In 1927 MATIGNON and MARCHAL[1] heated compacts of ignited beryllia mixed with excess calcium in alumina boats at temperatures above 800°C. They obtained only 25–33% reduction of the oxide.

## EXPERIMENTAL TECHNIQUE

The beryllium oxide was prepared by heating the hydroxide very slowly to 700°C, preliminary experiments[2] having shown that this produced a completely water-free material of maximum activity. Its only significant impurity was 0·9% of sodium fluoride. The calcium was a doubly distilled variety crushed and sieved to a size range of $-12 + 20$ mesh. Its only significant impurity was 0·5% of sodium chloride.

In a preliminary study of the reaction, compacts of beryllium oxide and calcium containing about 100% excess of calcium were heated to 1000°–1100°C in sealed containers. The reacted compacts were assumed to consist of beryllium, lime, excess calcium, and unchanged beryllium oxide, and were leached in dilute acetic acid to dissolve the calcium and lime. X-ray and chemical analysis showed that the leached products consisted predominantly of an alloy of calcium and beryllium, containing about 75% of the latter. No lines corresponding to beryllium, calcium, or their oxides were observed in X-ray powder photographs.

Further investigations of the reaction were facilitated by the construction of a horizontal argon-atmosphere tube furnace through which compacts of the reactants could be fed. In this way a reaction could be completed in one to two hours, instead of one to two days as in the "bomb" type of reaction.

It was desired to examine the beryllium calcium alloy in as pure a state as possible. For this purpose it was important that the reaction should go to completion, since beryllia unreacted at this stage would be extremely difficult to remove from the alloy at a later stage. The optimum conditions for complete reduction were therefore studied. The variables examined were the calcium content, the furnace temperature, and the time at this temperature. The calcium content was varied from the stoichiometric amount for the reaction $BeO + Ca \rightarrow CaO + Be$ to 120% in excess of this amount. Only two temperatures (900° and 1000°C) were tried, since the upper limit of the furnace was 1000°C,

[1] C. MATIGNON and G. MARCHAL *Compt. Rend.* **185**, 812 (1927).
[2] P. MURRAY and R. W. THACKRAY *A.E.R.E. M/R* 1410 (1954).

and it was found that the compacts would not react below about 850°C. The reaction of the beryllia with the calcium was easily visible. After the compact had been in the hot zone for about 30 seconds, a red glow appeared on the top edge, accompanied by the formation of white fumes of calcium vapour. This glow spread steadily through the compact, taking 15–45 seconds to reach the bottom edge. In the investigation of the effect of heating time the compacts were withdrawn from the hot zone at measured intervals after the red glow had spread right through them. Otherwise they were withdrawn 30 minutes after this moment. Since beryllia is only slowly and slightly soluble in dilute hydrochloric acid, the amount of beryllia left unreduced in each reacted compact was determined by dissolving the compact in this acid and weighing the insoluble residue.

A series of reactions were carried out under the optimum conditions for complete reduction as determined by these experiments. The products were hard greenish-grey cakes consisting of the beryllium-calcium alloy intimately mixed with excess calcium and lime. The alloy was readily soluble in dilute mineral acids but only slowly soluble in organic acids, and a leaching technique based on the use of acetic acid was developed. Experiment showed that the loss of alloy by solution was always appreciable (about 10%), but was considerably increased if the temperature was allowed to rise or if leaching times were unduly long. Optimum conditions for leaching 50-g batches of reaction product were as follows; acetic acid and crushed reaction product (in equivalent amounts) were added alternately to a stirred mixture of ice and water; 50 ml of excess acid were added and the suspension was stirred at a temperature of about 15°C until leaching was complete (about 30 min). It was finally filtered, washed in water, washed in ether, and vacuum dried. The recovery of alloy by this leaching technique was about 85–90%, the remaining 10–15% being lost by solution in the acetic acid. The complete removal of lime and excess calcium by leaching was difficult to prove, since the alloy contained calcium and also a little oxygen combined as BeO. X-ray analysis was the only suitable method, and X-ray powder photographs of the alloy leached under standard conditions did not reveal the presence of any calcium oxide. The X-ray method is insensitive, however.

Samples of the alloy prepared and leached in this way were examined by X-ray and chemical analysis. In addition attempts were made to remove the calcium from the alloy; the following methods of removal were examined:

### 1. *Vacuum Distillation*

If the calcium beryllium alloy were comparatively unstable, heating it to a fairly high temperature in vacuum might reasonably be expected to result in the calcium distilling off and leaving the beryllium behind, since the vapour pressure of pure calcium at all temperatures is very much higher than that of beryllium. 600-mg samples of the alloy were heated for 2 hr at 1200°C in a vacuum furnace at pressures of less than $2 \times 10^{-6}$ mm of mercury. Since the scale effect is most important in this type of surface controlled process, larger samples of 6 g weight were also heated for 2 hr at 1200°C.

### 2. *Hydriding*

Calcium reacts with hydrogen when heated to form $CaH_2$, whereas beryllium does not react in this way. Calcium hydride is not very stable, its dissociation pressures of hydrogen being:—

| $T$°C | 605 | 750 | 795 |
|---|---|---|---|
| $P_{H_2}$ (mm) | 28 | 410 | 854 |

If however $CaH_2$ were more stable than the beryllium-calcium alloy, one would expect the alloy to decompose in hydrogen to calcium hydride and beryllium, a circumstance which would be favoured by increasing the hydrogen pressure. Since $CaH_2$ is readily soluble in water or dilute acids, it should be possible to leach the calcium hydride from beryllium. Hydriding was attempted by heating the alloy in a stream of purified hydrogen at 1 atmosphere pressure, at temperatures from 500°–800°C. In a second series of experiments the alloy was heated to 700°–800°C. under a pressure of 23 atmospheres of hydrogen.

### 3. *Reactions with Other Metals*

Calcium forms the intermetallic compounds $Ca_2Mg_4$, $Ca_2Pb$, and $Ca_2Bi_2$. It is conceivable, therefore, that by heating the beryllium-calcium alloy with magnesium, lead or bismuth, the calcium would be removed by the formation of one of these compounds. The positions of the equilibria reached would depend on the relative stabilities of the calcium compounds. Separation of beryllium

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from the calcium compounds could possibly be accomplished in the case of $Ca_3Mg_4$ by leaching out the readily soluble compound from the beryllium with dilute acids, and in the case of the lead and bismuth compounds by melting the mixtures and using gravity separation of immiscible (?) liquids. The powdered alloy was therefore mixed with one of the aforementioned metals in the form of fine shreds or filings, and the mixture compacted into a pellet. The pellet was placed in a sealed, argon-filled crucible and heated to 800°C (Mg) or 900°C (Pb and Bi) for 1 hour.

## RESULTS AND DISCUSSION

The fact that beryllia and calcium did not react below 850°C suggested that the reaction was initiated when the calcium melted (851°C). In Figs. 1 and 2 the reaction variables investigated are plotted against the amount of residual unreacted beryllia. From these curves it was concluded that optimum conditions for as complete reduction as possible were that the compact should contain 100% excess of calcium, and should

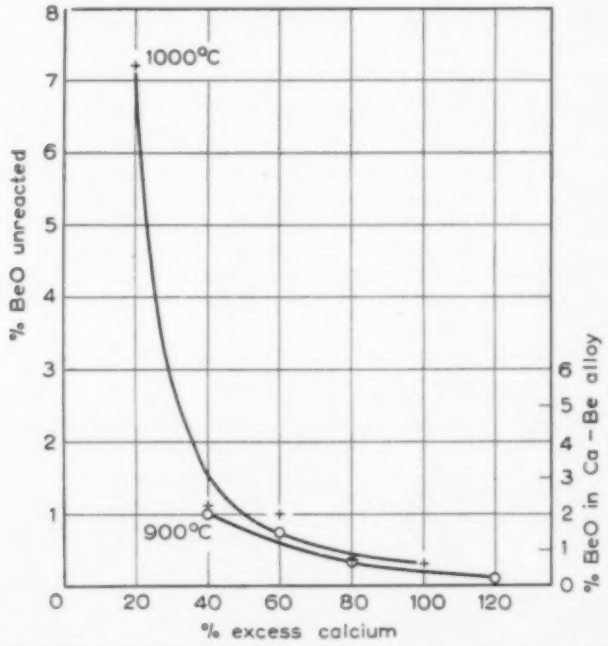


FIG. 1.—The effects of excess calcium and temperature on the completeness of reduction in the calcium reduction of beryllia.
+ Results at 1000°C.
○ Results at 900°C.

be soaked at 1000°C after reaction for about 15 minutes. The composition of the alloy prepared in this way was:

| Element | Be | Ca | F | Si | Fe |
|---|---|---|---|---|---|
| Wt.% | 73·4 | 25·6 | 0·09 | 0·12 | 0·04 |

It has been reported[3] that beryllium and calcium form an alloy of approximate composition 73% Be, 27% Ca (i.e. $CaBe_{12}$) and it was at first thought that the reaction product might consist mainly of this alloy. However, a detailed X-ray study was made

[3] W. KROLL and E. JESS *Wiss. Veröff., Siemens Konzern* **10**, (2) 29 (1931).
[4] T. W. BAKER and J. WILLIAMS *Acta Cryst.* **8**, (8), 519 (1955).

by BAKER and WILLIAMS; it has been reported elsewhere.[4] They showed the alloy to be a definite compound, $CaBe_{13}$, with a face-centred cubic structure of cell size 10·312 ± 0·001 Å, and isomorphous with other $MBe_{13}$ compounds. The chemical analysis closely approximated to $CaBe_{13}$ (74·5% Be, 25·5% Ca). The main impurities were fluorine and silicon, both derived from the beryllia.

None of the attempts to remove calcium from the alloy were successful. The vacuum distillation of 600-mg samples at 1200°C for 2 hr removed all but 2·1% of the calcium and a considerable quantity of beryllium from the alloy. However, the rate at which calcium was lost from the 6-g samples was less than that at which pure

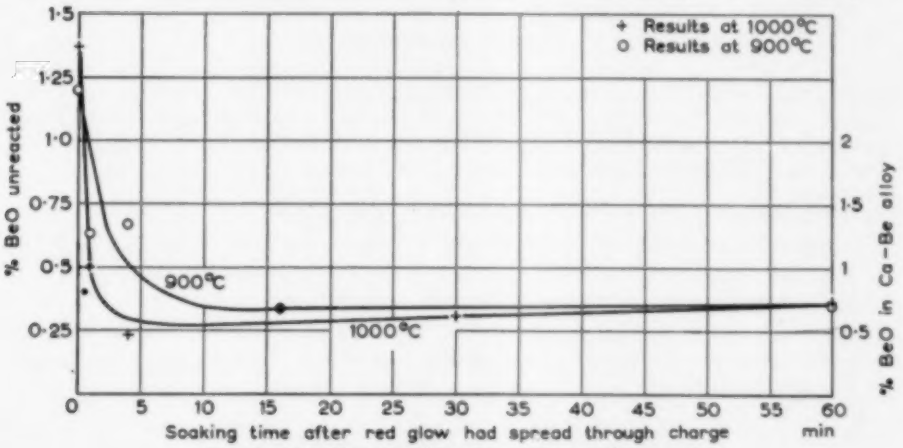


FIG. 2.—The effect of soaking time on the completeness of reduction in the calcium reduction of beryllia.
+ Results at 1000°C.
⊙ Results at 900°C.

beryllium distilled under identical conditions. X-ray examination of the samples treated in hydrogen at one atmosphere showed that they still consisted of $CaBe_{13}$ only. X-ray photographs of samples treated at 23 atmospheres of hydrogen did show a trace of calcium hydride. There is thus some indication that hydriding at very high pressures of hydrogen might be more successful. No reaction between $CaBe_{13}$ and magnesium, bismuth, or lead was detectable by X-ray methods.

The low free-energy change for the reaction $BeO + Ca \rightarrow Be + CaO$ has already been mentioned. The fact that the reaction $13BeO + 14\,Ca \rightarrow CaBe_{13} + 13CaO$ goes comparatively readily substantially to completion suggests that $CaBe_{13}$ is a compound of some stability. The negative results of the attempts to separate calcium from the alloy serve to confirm the stability of the compound.

*Acknowledgement*—This work was carried out in the Metallurgy Division of the Atomic Energy Research Establishment, and is published by permission of the Director. The authors would like to thank Dr. H. M. FINNISTON, the Chief Metallurgist at A.E.R.E., for many helpful discussions.



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# THE REACTION OF COBALT(II) BROMIDE WITH LITHIUM BOROHYDRIDE AND LITHIUM ALUMINOHYDRIDE

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**Abstract**—The reaction of cobalt(II) bromide with lithium borohydride gives a precipitate containing cobalt and boron in the mole ratio of 1/2 and hydrogen; with lithium aluminohydride a similar cobalt-aluminium precipitate and hydrogen are obtained. These precipitates are black, pyrophoric materials which exhibit chemical behaviour typical of the elements.

COBALT(II) bromide reacts with an excess of lithium aluminohydride to give four moles of hydrogen for each mole of cobalt(II) bromide and a black, pyrophoric precipitate which contains all the cobalt. If an excess of cobalt(II) bromide is employed, two moles of hydrogen for each mole of aluminohydride and a black, pyrophoric precipitate which contains all the aluminium are obtained. Regardless of the conditions, the results corresponded to the oxidation of an aluminohydride group to aluminium and hydrogen by an equivalent of cobalt:

$$CoBr_2 + 2LiAlH_4 = Co{\cdot}2Al + 2LiBr + 4H_2. \quad (1)$$

The precipitate[2] (Co·2Al) reacts with methyl alcohol to give three moles of hydrogen for each mole of cobalt and a black residue. This latter material, upon treatment with dilute acid, reacts to give one mole of hydrogen for each mole of cobalt. Assuming, as before (equation 1), that the original precipitate contained two moles of aluminium for each mole of cobalt, the successive treatments with alcohol and acid can be represented by the equations:

$$Co{\cdot}2Al + 6CH_3OH = Co + 2(CH_3O)_3Al + 3H_2 \quad (2)$$

and

$$Co + 2H^+ = Co^{++} + H_2. \quad (3)$$

Reaction of cobalt(II) bromide with lithium borohydride is similar in every respect to that with lithium aluminohydride:

$$CoBr_2 + 2LiBH_4 = Co{\cdot}2B + 4H_2 + 2LiBr. \quad (4)$$

The material Co·2B reacts with methyl alcohol:

$$Co{\cdot}2B + 6CH_3OH = 2(CH_3O)_3B + 3H_2 + Co. \quad (5)$$

It should be noted that the present study gives no indication of the nature of the precipitates Co·2B and Co·2Al. Their behaviour does, however, suggest an intimate

[1] Taken from a thesis submitted by ALBERT C. STEWART to the Graduate School of St. Louis University in partial fulfillment of the requirements of the degree of Doctor of Philosophy, June 1951. Most of the experimental work described herein was completed during 1947–1948 at the University of Chicago.
[2] The symbols Co·2Al represent only the empirical composition of the precipitate.

mixture of elements, similar to the previously described products[3] (Fe·2Al and Fe·2B) obtained in the reaction between iron(II) chloride and lithium alumino- and boro- hydrides.

Although the factors which determine the products of the reaction between anhydrous metal halides and alumino- or borohydride are undoubtedly complex, principal among these must be the strength of the metal halide as an oxidant. In sharp contrast to the oxidation of the alumino- or borohydride group by cobalt(II), oxidation by iron(III)[3] (reduced to iron(II)) or by silver(I)[4] gives aluminium hydride or diborane and hydrogen, while oxidation by copper(I)[5] or by iron(II)[3] proceeds by both routes, the first favouring the hydride and hydrogen; the second the element and hydrogen. Oxidation of lithium borohydride by cadmium(II) is reported[6] to give boron and hydrogen. Thus, the stronger oxidants, iron(III), copper(I), and silver(I), favour formation of the hydride and hydrogen, while the weaker oxidants, iron(II), cobalt(II), and cadmium(II), give the elements.

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## EXPERIMENTAL

The experimental methods employed in this work have been adequately described.[3] *Materials*: *Anhydrous cobalt (II) bromide* was obtained from the City Chemical Company of New York and its purity was established by analysis for bromide: calculated 73·1 %, found 72·9 %. *Lithium aluminohydride-ether solutions* were prepared by extraction of the commercial product (Metal Hydride Corporation) with anhydrous ether. The solutions were standardized from time to time by determination of active hydrogen, and their identity was confirmed by analysis for aluminium. Measured volumes were employed in the reaction with cobalt(II) bromide. *Lithium borohydride* was purified by recrystallization from diethyl ether.The purified material was pumped free of ether at 90° to 100°, two hours usually sufficing. The identity of the material was established by determination of active hydrogen and titration for boron. For a typical sample, 39·1 mg gave 153·5 c.c. hydrogen (calc. 160·0) and 40·1 c.c. boron (calc. 41·1) or a hydrogen-to-boron ratio of 3·90.

### *A. Reaction of Cobalt(II) Bromide with Lithium Aluminohydride*

To a weighed sample of cobalt(II) bromide was added a measured volume of lithium aluminohydride-diethyl ether solution while the reactor was maintained at −196°. The temperature of the reactor was slowly brought to room temperature whereupon a vigorous reaction, evolving hydrogen, occurred. From time to time the reactor was cooled to −196° and the hydrogen transferred by means of a Toepler pump to a measuring bulb. About 85 % of the total hydrogen was produced within the time required to perform the first measurement (about ten minutes) and the reaction appeared complete within two hours. The mixture was allowed to stand overnight to assure completion of the reaction. In those experiments in which an excess of cobalt(II) bromide was taken, examination of the solution after separation of the precipitate showed the absence of aluminium and active hydrogen, demonstrating that all of the lithium aluminohydride had reacted. With lithium aluminohydride

[3] G. W. Schaeffer, J. S. Roscoe, and A. C. Stewart *J. Amer. Chem. Soc.* **78**, 729 (1956).
[4] E. Wiberg and W. Henle *Z. Naturforsch.* **7b**, 250 (1952).
[5] R. H. Toeniskoetter, Master's Thesis, St. Louis University, January 1956; T. Klingen, Master's Thesis, St. Louis University, June 1955.
[6] E. Wiberg and W. Henle *Z. Naturforsch.* **7b**, 582 (1952).

in excess, all of the cobalt was recovered in the precipitate. The data so obtained are given in Table 1. The mole ratios of hydrogen to cobalt(II) bromide and lithium aluminohydride are in excellent accord with equation (1).

TABLE 1.—THE REACTION OF COBALT(II) BROMIDE WITH LITHIUM ALUMINOHYDRIDE

| $CoBr_2$ mmoles | $LiAlH_4$ mmoles | $H_2$ mmoles | $H_2/CoBr_2$ | $H_2/LiAlH_4$ |
|---|---|---|---|---|
| 0·74 | excess | 2·82 | 3·81 | — |
| 0·746 | excess | 2·85 | 3·82 | — |
| 0·383 | excess | 1·65 | 4·30 | — |
| excess | 1·17 | 2·32 | — | 1·99 |
| excess | 1·15 | 2·14 | — | 1·86 |
| | | | — | — |
| | | | 3·98 | 1·92 |

(1) *Reaction of* Co·2Al *with methyl alcohol.* Methyl alcohol was added directly to the reaction products obtained from the preceding experiments in which an excess of cobalt(II) bromide was employed; a vigorous reaction ensued producing hydrogen and leaving a black precipitate different in character from the initial material. The reaction product derived from 0·58 mmole of $CoBr_2$ produced 1·79 millimole of $H_2$ or a $H_2$/Co ratio of 3·09. Two further experiments gave mole ratios of 1·60/0·57 = 2·84 and 1·08/0·38 = 2·89. Thus the mole ratios of hydrogen to cobalt approach 3·0, that expected if the reaction observed is represented by equation (2), in conformity with the assumption that the original black precipitate contains two moles of aluminium for each mole of cobalt.

(2) *Examination of the cobalt precipitate.* The black precipitate, equivalent to 0·74 mmole (0·59 mmole) of $CoBr_2$, which remained after the methyl alcohol treatment just described was treated with dilute acid whereupon 0·75 mmole (0·59 mmole) hydrogen was evolved and the precipitate dissolved to give a pink solution. The ratio $H_2/CoBr_2$ is thus found to be 1·01 (1·00), that expected if the precipitate contained, as elementary cobalt, all that taken and if the cobalt was oxidized to cobalt(II) by the reaction with acid, equation (3).

*B. Reaction of Cobalt(II) Bromide with* $LiBH_4$

Weighed amounts of $CoBr_2$ and $LiBH_4$ were introduced into the reactor, the reactor was evacuated and 10 ml of anhydrous diethyl ether were condensed onto the reactants by means of liquid nitrogen. The reactants were then allowed to warm to room temperature. In contrast to the reaction with $LiAlH_3$, the black precipitate was not formed immediately but as the temperature of the mixture rose, a greyish-white solid was obtained which began to darken in a few minutes and, after about fifteen minutes, turned completely black. The intermediate material was not further investigated but, by analogy to other systems,[2] may be presumed to be a cobalt borohydride.

(1) *Hydrogen produced at room temperature.* As soon as the intermediate grey-white solid began to darken, hydrogen was evolved. From time to time the reactants were frozen with liquid nitrogen and the hydrogen transferred to the vacuum apparatus

for measurement. About 85% of the hydrogen was produced within a few minutes after the reaction attained room temperature but the reactor was allowed to stand overnight to assure completion of the reaction. The data obtained in this manner are recorded in Table 2.

TABLE 2.—THE REACTION OF COBALT(II) BROMIDE WITH LITHIUM BOROHYDRIDE

| $CoBr_2$ mmoles taken | $LiBH_4$ mmoles taken | $H_2$ mmoles | $H_2/CoBr_2$ | B mmoles in ppt | $B/CoBr_2$ |
|---|---|---|---|---|---|
| 0·358 | 1·82 | 1·41 | 3·95 | — | — |
| 0·354 | 1·72 | 1·44 | 4·08 | 0·132 | 2·06 |
| 0·518 | 2·76 | 2·05 | 3·95 | 1·04 | 2·01 |
| 0·231 | excess | — | — | 0·441 | 1·91 |
| | | | — | | — |
| | | | 3·99 | | 2·00 |

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(2) *Composition of the precipitate.* The black precipitate was filtered and washed free of ether soluble materials (lithium borohydride and, in part, lithium bromide). The precipitate was taken up in dilute acid, in which it dissolved with the evolution of hydrogen, and the solution was analysed for boron. The results are given in Table 2, column 5. The ratios $H_2/CoBr_2$ (column 4) and $B/CoBr_2$ (column 6) are both in agreement with equation (5). Because all of the cobalt remained in the precipitate, the composition of the precipitate may be taken as Co·2B.

(3) *Reaction of* Co·2B *with methyl alcohol.* In two cases the black precipitate was filtered and washed with ether and then, before the determination of boron was carried out, it was allowed to react with 10 ml methyl alcohol and the hydrogen, 1·00 mmole (1·56 mmole), was produced. If the amount of Co·2B, 0·384 mmole (0·518 mmole) is assumed to be equal to the amount of $CoBr_2$ originally employed, the ratio of hydrogen to Co·2B is 2·82 (3·00), a value which is in accord with equation (5). A black precipitate, identical in appearance and behaviour to that observed after treatment of the Co·2Al, remained but it was not examined further.

(4) *Amount of lithium borohydride reacting.* Cobalt(II) bromide (0·354 mmole) was reacted with 1·72 mmoles of lithium borohydride. Upon completion of the reaction, the residue was washed free of unreacted lithium borohydride and the ether washings were analysed for boron (0·84 mmole found) and hydrogen (3·15 mmoles found). The ratio of hydrogen to boron (3·15/0·84 = 3·75, theory 4·00) is that expected if the ether-soluble material were the unreacted borohydride. The amount of lithium borohydride recovered (0·84 mmole) compares satisfactorily with the expected excess (1·01 mmole) calculated on the basis of equation (4) and considering that the technique employed did not permit complete recovery of the ether-soluble fraction.

*Acknowledgements*—One of us (A. C. S.) gratefully acknowledges the support provided through the Office of Naval Research during his tenure at the University of Chicago. The continued interest and encouragement of Professor H. I. SCHLESINGER are deeply appreciated.

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# ALIZARIN SULPHONATE COMPLEXES OF ZIRCONIUM AND HAFNIUM

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**Abstract**—The reaction of alizarin S with dilute ($10^{-4}$ M) zirconium and hafnium solutions in 0·1 M $HClO_4$ was studied amperometrically. An insoluble compound formed initially but redissolved upon the addition of excess metal ion. The stoichiometry for these two species depended upon the age of the metal ion solution. The mole ratio of zirconium to alizarin S at the first end point increased from 0·8 to 1·0 as the solution aged and for hafnium from 0·81 to 0·88 over the same period. For the second end point, the ratio ranged from 1·2 to 1·75 for zirconium and remained constant at 1·2 for the hafnium solutions. The ultra-violet and visible absorption spectra of aqueous solutions of these two compounds were the same. From the amperometric and spectral data it was concluded that the metal was chelated by a quinoid oxygen and the alpha phenolic oxygen. Solubilization of the initial precipitate probably involves the reaction of additional metal ions with the chelated metal.

THE reaction of alizarin or alizarin S with zirconium and hafnium in aqueous or alcohol solution has long been used as the basis for the colorimetric quantitative estimation of these elements. A wide variety of conditions have been prescribed[2–10] with each procedure set up on an empirical basis.

Several attempts have been made using spectrophotometric methods to explore the stoichiometry of this reaction,[7, 11–14] the general conclusion (with the exception of MAYER and BRADSHAW's) being that the metal to alizarin (alizarin S) ratio is one. These investigations all suffer from the limitations of the method used, namely, that the spectrophotometric method is not suitable in regions where precipitation occurs, nor can it be used to investigate species of very similar absorbancy. By using a polarographic method for the study of this reaction, these difficulties were circumvented.

## EXPERIMENTAL

*Apparatus.* The polarographs used in this work were: manual polarograph, Sargent Model III, sensitivity 0·0059 $\mu$A per mm.; and a photorecording polarograph, Sargent Model XII, sensitivity 0·0047 $\mu$A per mm. The capillary constants of the dropping mercury electrode were 1·47 (5) at 0 volt, 1·50 at −0·25 volt, and 1·51 at −0·5 volt.

[1] Based on a thesis submitted by Stanley Hirozawa in partial fulfilment of the requirements for the degree of Doctor of Philosophy. This work was supported in part by the Office of Naval Research.

[2] J. H. DE BOER *Chem. Weekblad* **21**, 404 (1924).
[3] D. E. GREEN *Analyt. Chem.* **20**, 370 (1948).
[4] J. C. GRIESS, JR. *U.S. Atomic Energy Comm. AECU* 129 (1949).
[5] R. GRUENTHER and R. H. GALE *U.S. Atomic Energy Comm. KAPL* 305 (1950).
[6] H. A. LIEBHAFSKY and E. H. WINSLOW *J. Amer. Chem. Soc.* **60**, 1776 (1938).
[7] A. MAYER and G. BRADSHAW *Analyst* **77**, 476 (1952).
[8] PEI WANG Ph.D. Thesis, University of Wisconsin (1951).
[9] G. B. WENGERT *Analyt. Chem.* **24**, 1449 (1952).
[10] D. L. MANNING and J. C. WHITE *ibid* **27**, 1389 (1955).
[11] H. A. LIEBHAFSKY and E. H. WINSLOW *J. Amer. Chem. Soc.* **69**, 1130 (1947).
[12] J. F. FLAGG, H. A. LIEBHAFSKY, and E. H. WINSLOW *ibid* **71**, 3630 (1948).
[13] Y. DORTA-SCHAEPPI, H. HURZLER, and W. D. TREADWELL *Helv. Chim. Acta* **34**, 797 (1951).
[14] O. GÜBELI and A. JACOB *ibid* **38**, 1026 (1955).

A sodium perchlorate bridge was used in place of the usual potassium chloride bridge to prevent the precipitation of potassium perchlorate and to avoid chloride contamination. A saturated sodium chloride solution served to connect the bridge to the saturated calomel electrode. All titrations were carried out in a constant-temperature bath at 25·00 ± 0·05°.

The Cary recording spectrophotometer was used for the spectral studies.

*Materials*. The commercial alizarin S available contained about a 25% sulphate impurity. The crude alizarin S was extracted with hot, 50% ethanol, the residue discarded, and the product crystallized by cooling. The sulphate-free material, analysed potentiometrically and amperometrically, gave a combined alizarin–alizarin S content of 98·9%, with 94·7% alizarin S. Although the material still contained some free alizarin it was used as such. The stock solution was made up in 0·1 M perchloric acid and the total quinoid oxygen content determined. The concentrations were expressed as moles of alizarin S + alizarin per litre, since both species react similarly with the metal ions. The concentrations of the solutions ranged from $3{\cdot}4 \times 10^{-5}$ to $3{\cdot}4 \times 10^{-4}$ mole/litre.

Zirconium and hafnium oxychloride samples were available in this laboratory. The hafnium content of the zirconium sample was 0·3 mole %, and the zirconium content of the hafnium sample was 0·7 mole %. The atomic weights were corrected accordingly.

The zirconium and hafnium stock solutions were made up in the following manner. To a sample of the oxychloride was added 60% perchloric acid, and the mixture heated until the solution was chloride free. The perchloric acid lost in the process was replaced, the solution transferred to a volumetric flask and diluted with distilled water. The amount of perchloric acid originally used was that, which upon dilution gave about a 1 M solution. The metal-ion concentration in these stock solutions was about $5 \times 10^{-2}$ M.

The zirconium (hafnium) stock solutions were diluted to give solutions which ranged from $4 \times 10^{-3}$ M to $9 \times 10^{-5}$ M, in 0·1 M perchloric acid. When used immediately after dilution, these solutions are referred to as fresh solutions. When allowed to stand before using, the diluted solutions are referred to as aged, and the number of days of ageing are designated.

*Analytical Methods*. All the zirconium and hafnium stock solutions were standardized by precipitating the hydrous oxide with freshly prepared silica-free aqueous ammonia, and igniting the precipitate at 900°.

The alizarin S stock solution was standardized by titrating the quinoid groups amperometrically with titanium (III) chloride. The latter in turn was standardized amperometrically against a primary standard dichromate solution. The procedures for these two titrations were specially developed for this work.

The acid concentration of the metal-ion solutions was determined by titrating with standard sodium hydroxide to the bromthymol-blue endpoint in the presence of fluoride to complex the metal ion.[18]

*Procedure*. A preliminary "polarographic" titration of alizarin S with zirconium and hafnium was carried out with the photo-recording polarograph. Solutions of varying alizarin S to metal ion ratios were used, ranging from excesses of alizarin S to excesses of metal ion. There was a slight negative shift in the $E_{1/2}$ of the reaction product (−0·29 volt) compared to that of the free alizarin S (−0·25 volt). In the range of solution compositions used, the polarograms showed a region of diffusion current common to all over a fair voltage range. In subsequent amperometric titrations, a constant voltage of −0·5 volt was used.

All titrations were carried out with the manual polarograph. Great care was taken to wait until a steady current reading was obtained before the next increment of reagent was added. The current was recorded as centimetres of galvanometer deflection. A shunt ratio of one was used in all cases.

The solutions were stirred and deoxygenated with a stream of nitrogen. The water pumped tank nitrogen had been deoxygenated by passing over hot copper turnings at 425°.

Visible and ultra-violet absorption spectra were obtained on solutions whose compositions approximately corresponded to the endpoints determined in the amperometric titrations. Mixtures in which any precipitate was present were centrifuged and the supernatant liquids were used for the spectral studies. Some ultra-violet spectra were also taken in alcoholic solutions. These were prepared by evaporating at room temperature, 5 ml of a particular aqueous solution down to a few drops, and then adding about 5 ml of 95% ethanol.

[18] A. J. Zielen U.S. Atomic Energy Comm. UCRL-2268 (1953).

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*Amperometric Titration Results.* When alizarin S was titrated amperometrically with freshly prepared zirconium (hafnium) solutions, the first reaction line was curved (Fig. 1, *A*). This indicated that two reactions were taking place. From the time it took for a steady-state current to be obtained the initial reaction appeared to be rapid, and the second reaction appeared to be slow. The total current decreased to a sharp minimum at a metal ion to alizarin S ratio of about 0·83. The solution remained clear up to this addition of 1 ml of zirconium solution. Between 1 ml and the endpoint the solution gradually became turbid and finally the precipitate coagulated at the endpoint. For solutions of the same age and composition the average deviation of the endpoint was 0·8%. Upon the addition of more metal ion, the precipitate slowly went into solution. Simultaneously, the current increased and then levelled off at about one-half of the original current of the free alizarin S. The endpoint here was so broad the stoichiometry could not be determined. Zirconium and hafnium showed the same behaviour.

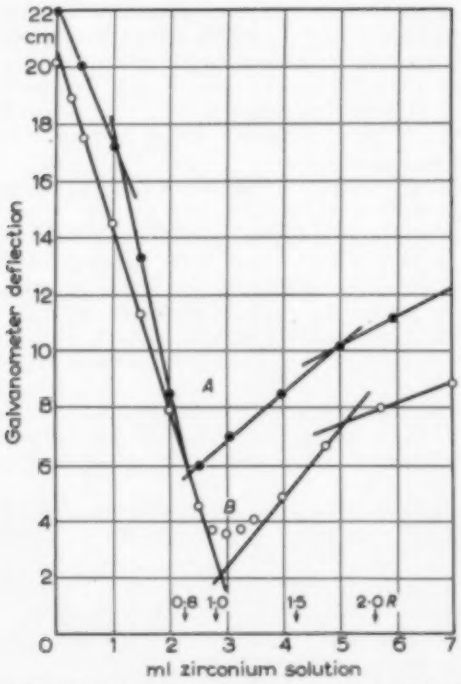



Fig. 1.—Forward titration in 0·1 M $HClO_4$. Forty ml, 3·43 × $10^{-4}$ M alizarin S titrated with fresh (*A*), with 22-day-old (*B*) zirconium solution.

As the diluted stock solutions of the metal ions aged, the first reaction line straightened out, and the minimum at the endpoint became round rather than sharp (Fig. 1, curve *B*). After 30 days the slow reaction had disappeared completely, and the reaction was fast all the way to the endpoint. The constant slope showed that only one reaction was taking place.

The important difference between the fresh and aged solutions was that the ratio of metal to alizarin S at the endpoint ($R_t$), increased with age from 0·83 to 1·00 (Fig. 3, Curve 2) or slightly greater for the zirconium solutions, and from 0·81 to only 0·88 for the hafnium solutions (Fig. 3, Curve 1). The hafnium solutions aged differently than the zirconium solutions in that they levelled off with a smaller constant $R_t$ value in a shorter time than the zirconium solutions did.

It was found that the ageing of the metal ion solution in 1–2 M perchloric acid had no effect on the stoichiometry at the endpoints. For example, when the diluted zirconium reagent was prepared from a freshly prepared zirconium solution in 1 M perchloric acid, the stoichiometry at the endpoint

was 0·84. When the titration was repeated with a freshly diluted stock from the same primary stock 8 days later, the stoichiometry at the endpoint was again 0·84. In another example, the freshly diluted zirconium reagent prepared from a 3-day-old stock solution in 2 M perchloric acid, gave a stoichiometry at the endpoint of 0·82, while the zirconium reagent prepared from the same primary stock 40 days later gave the same stoichiometry, 0·82.

The stoichiometry for the point at which the precipitate went into solution could not be ascertained from the forward titrations described above because of the gradual break in the titration curve. It was possible to determine this endpoint, however, by running a reverse titration, i.e. by titrating the metal ion with alizarin S (Fig. 2, *A*, *B*). Since the metal ions were not electroreducible at −0·5 V the current started at a low value and gradually rose to a maximum as the soluble complex was formed.

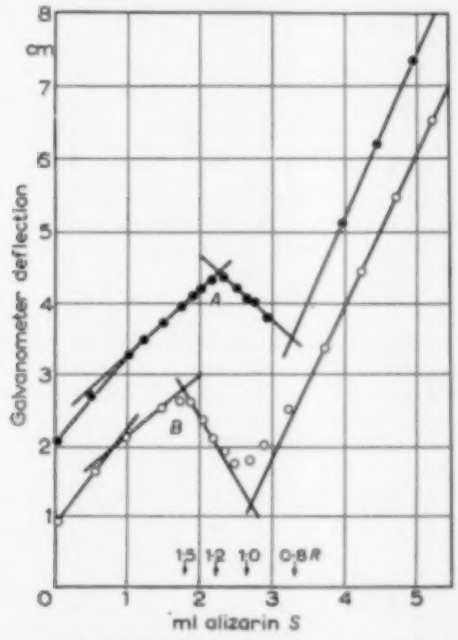



FIG. 2.—Reverse titration in 0·1 M $HClO_4$. Fifty ml of $9{\cdot}83 \times 10^{-4}$ M fresh (*A*), and 33-day-old (*B*) zirconium solutions titrated with $1{\cdot}71 \times 10^{-3}$ M alizarin S.

Upon the addition of more alizarin S the insoluble complex began to form and the current decreased to a minimum, only to rise again with the presence of excess uncombined alizarin S. In Fig. 2, *A* and *B* are reverse titration curves for fresh and aged zirconium (hafnium) respectively. Excellent agreement was obtained for the stoichiometry of the insoluble complex between the reverse and forward titrations for a solution of a given age (Fig. 3). This indicated that the reaction was reversible, and that adsorption phenomena did not play a role in determining the apparent stoichiometry.

The mole ratio of metal ion to alizarin S in the soluble complex changed with the age of the solution only in the case of the zirconium solutions. It varied from about 1·2 to 1·75 for the zirconium solutions (Fig. 3, Curve 4), while for the hafnium it remained constant at about 1·22 (Fig. 3, Curve 3) These solutions remained clear and showed no Tyndal beam.

From the observations made here on separate solutions there would appear to be some difference in the ageing process of zirconium and hafnium. This difference probably could not be utilized for the separation or for analytical purposes because there is evidence that these ions form mixed polymers.[16]

[16] EDWIN M. LARSEN and PEI WANG *J. Amer. Chem. Soc.* **76**, 6223 (1954).

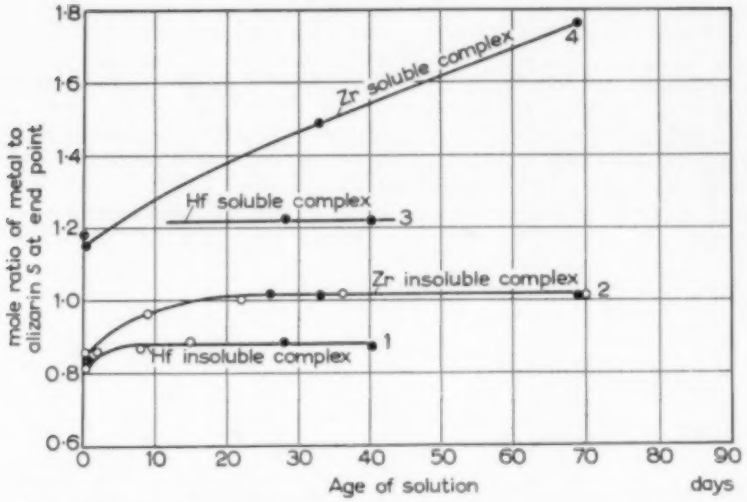



FIG. 3.—Effect of age of metal ion solution on the mole ratio of metal to Alizarin S at the end-point. Open circles forward; closed circles reverse titration.

## *Absorption Spectra*

*Alizarin S.* The visible absorption spectrum of a $10^{-3}$ M alizarin S solution at *p*H 4 or lower, consists of a single maximum at about 420 m$\mu$ (Fig. 4, curve *A*). Upon half neutralization with base, the peak shifts to a single maximum at 525 m$\mu$ (Fig. 4, curve *C*), which is the same as that for the metal alizarin S complexes. The half neutralization point is *p*H 8·3 as calculated for the $pK_1 = 5{\cdot}54 \pm 0{\cdot}01$ and $pK_2 = 11{\cdot}01 \pm 0{\cdot}04$ as determined by SACCONI[17]

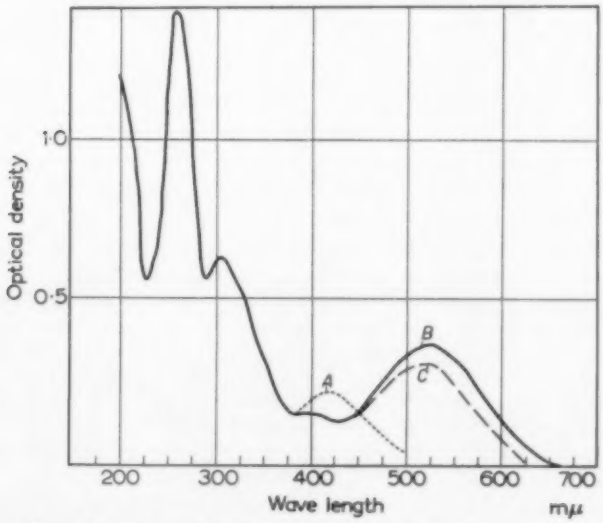



FIG. 4.—Absorption spectra. Solid line, Metal-Alizarin S complexes in aqueous solution; short dashed line, Alizarin S, acid solution; long dashed line, Alizarin S *p*H-8.

[17] L. SACCONI *J. Phys. Colloid Chem.* **54**, 829–41 (1950).

*Metal-Alizarin S Complexes.* The visible and ultra-violet spectrum of an aqueous solution of the soluble complex (Fig. 4 curve *B*) was essentially the same as that of a saturated solution of the insoluble complex. The only exception was the case in which a large excess of the metal ion was present, and then the 525 m$\mu$ peak was shifted to a slightly lower wavelength as is shown in Table 1. Only slight differences between the spectra of the complex formed from aged and fresh metal-ion solutions are noted. Since the spectrophotometric method does not distinguish between solutions of the soluble and insoluble complex, nor between fresh and aged solutions, even though the stoichiometries do differ, the results from such investigations should be re-examined. The spectra of the zirconium and hafnium complexes were the same.

TABLE 1.—$\lambda_{max}$ VALUES OF ALIZARIN S-METAL AQUEOUS SOLUTIONS

| Approximate metal/alizarin S mole ratio | m$\mu$ | |
|---|---|---|
| | Fresh | Aged |
| 0·80 | 261<br>307<br>524 | 261<br>307<br>521 |
| 1·00 | <br><br>525 | 263<br>304<br>522 |
| 1·2–1·75 | 261<br>307<br>525 | 262<br>307<br>525 |
| 2 | 261<br>307<br>517 | 262<br>306<br>513 |

### *Observations on the Solid Complexes*

Although spectrally there appeared to be no differences between the solutions of the reaction products resulting from the aged or fresh metal-ion solutions, some differences were observed in other properties of these compounds. For example, the insoluble solid recovered from a fresh metal-ion solution sublimed when heated at a controlled rate, whereas the insoluble compound recovered from the aged metal-ion solution, when heated under identical conditions, decomposed to the oxide and volatile organic products. In addition, although the solubility of these compounds in cyclohexane was very slight, the compounds prepared from the fresh metal-ion solutions were more readily extractable by the cyclohexane than those prepared from the aged metal-ion solution.

## DISCUSSION

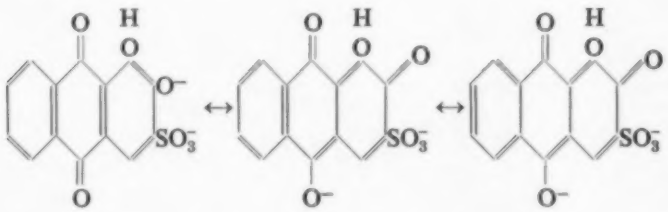
Earlier investigators[3, 7, 11, 12] reported metal ion to alizarin S (alizarin) ratios of about 0·8. Some[11, 12] considered this to be close enough to 1 to call it that; others[13, 14] claimed to have found a ratio of 1 by the method of continuous variations. It would appear, however, that this value of 0·8 and other non-integral values are real, and that they are related in part to the polymerization of the metal ion, It is not possible to draw a clear picture of the nature of the species formed because of lack of information on the nature of the metal ion in 0·1 M perchloric acid. On the basis of the work done at $10^{-3}$ M metal ion in 1 and 2 M perchloric acid,[15] and in

0·1 M perchloric acid[18] at metal ion concentrations of 0·05 M, it may be assumed that polymers containing as many as four metal atoms per unit are present in the solutions used here.

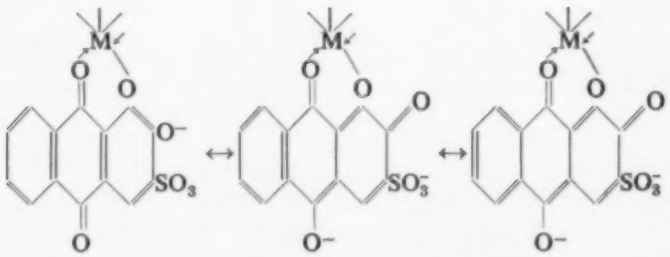
The ratio of 0·8 for the fresh insoluble compound corresponds to the simple whole number ratio of 4/5. Upon ageing of the zirconium solutions at least, this ratio became unity. Why there should be on the average, one more alizarin S molecule than metal ion in the solid cannot be explained by our data. Similarly for the fresh soluble complex the mole ratio of 1·2 corresponds to the simple whole number ratio of 6/5. Apparently as the insoluble unit goes into solution two metal ions are taken up per 4/5 unit. The zirconium compound at least, shows the tendency to take up more metal atoms per unit as the metal-ion solution is aged. This tendency is probably related to a greater extent of polymerization of zirconium compared to hafnium in 0·1 M perchloric acid.

Although the data cannot explain the nonintegral mole ratios, they do shed some light on the point of attachment of the metal in the alizarin S molecule. In the reaction of alizarin S with metal ions there are two possible positions which the metal ion may occupy: (1) the metal ion may be chelated by the pair of phenolic oxygens, or (2) the metal ion may be chelated by a quinoid oxygen and the alpha phenolic oxygen.

When alizarin S is half neutralized, the $\lambda_{max}$ in the visible is shifted from 419 to 525 m$\mu$. This shift in the $\lambda_{max}$ may be attributed to the removal of the beta hydrogen, thus enhancing resonance in the molecule.



A practically identical shift is observed when the metal ion reacts with alizarin S. If chelation is through the quinoid and alpha phenolic oxygen, then resonance similar to that above is possible.



If, however, the metal ion was chelated by the two phenolic oxygens, resonance as expressed above would not be possible, and one would not expect the correspondence

[18] KURT A. KRAUS and JAMES S. JOHNSON *J. Amer. Chem. Soc.* **75**, 5769 (1953).

in the $\lambda_{max}$ shift noted above. Thus the spectral evidence points to the chelation of a metal ion through the quinoid and alpha phenolic oxygen.

Polarographic evidence also points to the bonding of a metal atom by a quinoid oxygen and the alpha phenolic oxygen. In the forward amperometric titrations, as the insoluble compound dissolved upon the addition of excess metal ion, the current increased and approached a constant value which was slightly less than one-half the original current of the alizarin S. (Fig. 1, *A* and *B*). It was shown in the present work that the electrode reaction of the alizarin S involved a 2-electron reduction of the two quinoid groups. The approximate halving of the current upon complexing is evidence for the participation of a quinoid oxygen in compound formation, thus preventing its reduction under the conditions of the experiment. Had the metal ion been chelated by the phenolic oxygens, the current should have approached a value only slightly less than the original.

When two solutions have the same absorption spectra it is reasonable to assume that the same absorbing species are present in both solutions. However, in the case of the saturated solution of the insoluble complex, and the solution of the soluble complex this assumption does not seem reasonable. This can be explained if the solubilization reaction involves bonding between metal ions only, which has no effect on the resonance of the chromophoric group.

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*Acknowledgement*—We express our appreciation to Dr. IRVING SHAIN of this Department for the many helpful discussions concerning this work.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 206 to 214. Pergamon Press Ltd., London

# CHARGE TRANSFER RATES BETWEEN THE ETHYLENEDIAMINETETRA-ACETATE COMPLEXES OF Co(II) AND Co(III), AND OF Fe(II) AND Fe(III)

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(*Received* 31 *May* 1956)

**Abstract**—The charge transfer process was found to be immeasurably fast for the system $FeY^{-2}$—$FeY^{-1}$ (Y denoting the ethylenediaminetetra-acetate ligand), and, for the system $CoY^{-2}$—$CoY^{-1}$, to obey second-order kinetics with a specific rate constant of 0·75 $hr^{-1}M^{-1}$ at 85°C and *p*H 2. The energy and entropy of activation were found to be 22 kcal/mole and −17 cal/deg.mole, respectively.

It is suggested that this difference in lability of seemingly similar systems is explainable primarily in terms of their crystal-field energy-level diagrams and that other charge transfer cases can be correlated similarly.

## INTRODUCTION

A CHARGE transfer process is generally supposed to occur when identity interchange takes place between two species of the same chemical stoichiometry and differing in charge by one unit. A number of systems have been studied in aqueous media.[1] In several cases the exchange rates are quite small and various explanations have been suggested. The Coulomb energy of bringing ions of like charge together could constitute an important factor, depending upon the value assumed for the local dielectric constant.[2, 3] The charge factor does not seem to be controlling, however, in view of the rapidity of exchange between $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ and between $Mo(CN)_8^{-4}$ and $Mo(CN)_8^{-3}$[4, 5] WEISS's suggestion[6] of oxygen catalysis as a variable factor could not be confirmed in the case of the rapid but measurable exchange between $Fe^{+2}$ and $Fe^{+3}$[7]. LIBBY[8] pointed out that the electron transfer *per se* must be adiabatic in that no atomic motions can occur in the time interval involved, and concluded that to avoid excessive energy barriers the structures of the hydrated or co-ordinated ions in the two valence states should be the same within the amplitude of their zero point vibrations. It is not easy on this basis, however, to see why the exchange between $Eu^{+2}$ and $Eu^{+3}$ should be so vastly slower[9] than that between $Fe^{+2}$ and $Fe^{+3}$. LIBBY also noted that ions need not approach too closely for significant overlap of orbitals to occur, and MARCUS *et al.*[10] proposed a treatment which assumed the problem to be one of electron tunnelling.

[1] A. W. ADAMSON *J. Phys. Chem.* **56**, 858 (1952).
[2] J. W. COBBLE and A. W. ADAMSON *J. Amer. Chem. Soc.* **72**, 2276 (1950).
[3] M. H. GORIN *ibid.* **58**, 1794 (1936).
[4] A. C. WAHL and C. F. DECK *ibid.* **76**, 4054 (1954).
[5] R. L. WOLFGANG *ibid.* **74**, 6144 (1952).
[6] J. WEISS *J. Chem. Phys.* **19**, 1066 (1951).
[7] L. EIMER, A. I. MEDALIA, and R. W. DODSON *J. Chem. Phys.* **20**, 743 (1952).
[8] W. F. LIBBY *J. Phys. Chem.* **56**, 863 (1952).
[9] D. J. MEIER and C. S. GARNER *J. Amer. Chem. Soc.* **56**, 853 (1952).
[10] R. J. MARCUS, B. J. ZWOLINSKI and H. EYRING *J. Phys. Chem.* **58**, 432 (1954).

From an empirical point of view, it has been difficult to be sure what factors are important. The purpose of the present investigation was to study the effect of changing the central metal ion, keeping other factors, such as net charge and nature of the first co-ordination sphere, constant. The ethylenediaminetetra-acetate complexes of iron and cobalt were chosen with this goal in mind; the pairs $FeY^{-2}$—$FeY^{-1}$ and $CoY^{-2}$—$CoY^{-1}$ (Y denoting the ethylenediaminetetra-acetate ligand) are formally identical except for the metal ions.

## EXPERIMENTAL

### *Materials*

Iron 55–59 was converted to the trichloride, purified by ether extraction, and from this a stock solution of $FeY^{-1}$ was prepared by the addition of a slight excess of aqueous $Na_2H_2Y$. Solid $KCoY \cdot 2H_2O$ was prepared according to the method of SCHWARZENBACH and FREITAG[11] using $Co^{60}$(II) nitrate. The radioisotopes were obtained from the Isotopes Division of the United States Atomic Energy Commission.

Solutions containing ferrous iron were prepared from ferrous ammonium sulphate, and, in general, analytical grade reagents were employed.

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### *Exchange between* $FeY^{-2}$ *and* $FeY^{-1}$

The exchange systems were made up by adding excess aqueous $Na_2H_2Y$ to a solution of labelled Fe(III), followed by the addition of excess Fe(II), the *p*H of each component having been previously adjusted to 2 by the addition of hydrochloric acid. Since the exchange between $Fe^{+2}$ and $FeY^{-2}$ is rapid,[12] the course of the exchange could be followed by determining the specific activity of the excess $Fe^{+2}$. The first separation method employed consisted of adding an ammonium chloride-ammonium hydroxide buffer; the actual precipitate was ferric hydroxide, due to the oxidizing action of the $FeY^{-1}$.

An alternative separation method consisted of passing the exchange solution rapidly through a Dowex 50 cation-exchange column (using the sodium form). Ferrous ion was retained and could then be eluted separately. Iron containing solutions were analysed by the method for FORTUNE and MELLON[13] and counted by means of a scintillation counter.

### *Exchange between* $CoY^{-2}$ *and* $CoY^{-1}$

The general procedure was similar to that described above. Solutions for the exchange runs were prepared by mixing appropriate amounts of stock solutions of labelled KCoY, $Na_2H_2Y$, and cobaltous nitrate, and then adjusting the *p*H with either nitric or perchloric acid (it proved to be immaterial as to which acid was employed). The stoppered volumetric flask containing the mixture was then placed in a thermostat and samples were withdrawn periodically for analysis. In some cases excess cobaltous ion was present in the initial exchange mixture, while in others $Na_2H_2Y$ was initially in excess, and additional cobaltous nitrate was added just prior to separation.

The ion exchange separation method described above was used, and cobalt containing solutions were analysed by the method of CARTLEDGE and NICHOLS[14] and their radioactivity determined by means of a well-type scintillation counter. As in the case of the iron system, exchange is rapid between $Co^{+2}$ and $CoY^{-2}$[15] so that the specific activity of the two could be equated.

## EXPERIMENTAL RESULTS

Complete exchange was found to occur between $FeY^{-2}$ and $FeY^{-1}$ at 20°C, within the separation time of *ca.* 15 seconds and using either separation method. In connection with the first separation procedure, involving the addition of a buffer to

[11] G. SCHWARZENBACH and E. FREITAG *Helv. Chim. Acta* **32**, 839 (1948).
[12] S. S. JONES and F. A. LONG *J. Phys. Chem.* **56**, 25 (1952).
[13] W. B. FORTUNE and M. G. MELLON *Ind. Eng. Chem. (Anal)* **10**, 60 (1938).
[14] G. H. CARTLEDGE and P. M. NICHOLS *Ind. Eng. Chem. (Anal)* **13**, 20 (1941).
[15] F. A. LONG S. S. JONES, and M. BURKE *Chem. Abs.* **45**, 4166 (1951).

precipitate ferric hydroxide, it was possible that exchange was induced either by contact catalysis or as a result of the redox process (1) which occurred.

$$Fe^{+2} + FeY^{-1} + 3OH^- = Fe(OH)_3 + FeY^{-2} \quad (1)$$

However, addition, just prior to separation, of aqueous tri-iodide ion, which oxidized the $FeY^{-2}$, or of aqueous bromine, which also oxidized the free ferrous ion, also resulted in complete exchange. Precipitation of ferric hydroxide does not induce exchange between $Fe^{+3}$ and $FeY^{-1}$ [12] so that it seemed likely that the rapid exchange observed here was not catalysed. The similar results, when the ion exchange-separation

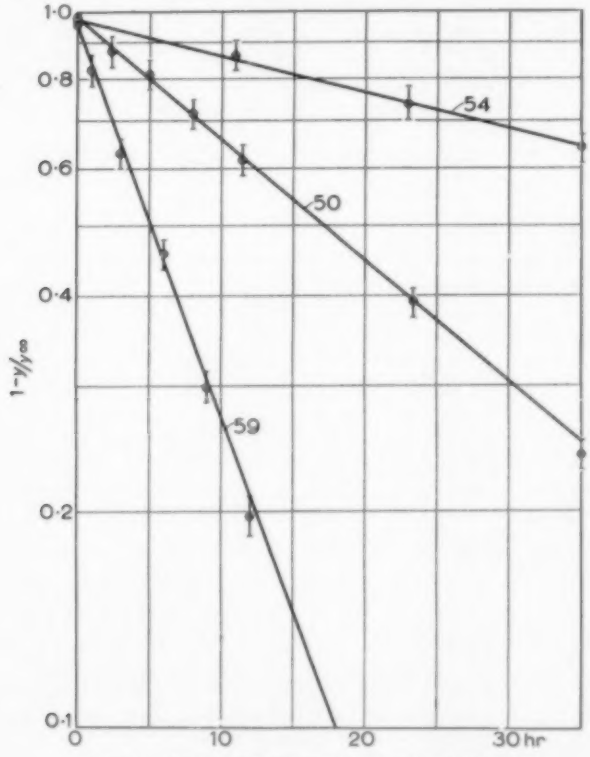


FIG. 1.—Exchange between $CoY^{-2}$ and $CoY^{-1}$ at 85°C.

method was employed, again seem reliable, in view of the success of this method with the cobalt system.

Exchange between $CoY^{-2}$ and $CoY^{-1}$ was found to be slow, and data were obtained mostly at $85 \pm \cdot 2$°C. Straight lines were obtained with McKAY[16] type plots, as illustrated in Fig. 1. The results are summarized in Table 1. The rate, $R$, of the process leading to exchange was computed from the slope, $c$, of the McKay plot by means of the relationship $c = R(1/a \times 1/b)$, where $a$ and $b$ are the total concentrations of Co(II) and Co(III). The second-order rate constant was then given by $R = k_{2nd}(a')(b)$, where $a'$ and $b$ now denote the concentrations of $CoY^{-2}$ and $CoY^{-1}$, respectively.

[16] H. A. C. McKAY *Nature* **142**, 997 (1938).

TABLE 1.—EXCHANGE BETWEEN $CoY^{-2}$ and $CoY^{-1}$

| Run | $t$°C | $p$H[a] | *Concentrations*[b] (moles/l) | | | $Y$ | $T_{1/2}$ (hr) | $k_{2nd}$ ($hr^{-1}M^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | $CoY^{-2}$ | $CoY^{-1}$ | $Co^{+2}$ | | | |
| | | | *Order with respect to* $CoY^{-2}$ | | | | | |
| 19 | 85 | 2·0 | ·0180 | ·0163 | ·0219 | ·000 | 65·7 | ·49 |
| 20 | 85 | 2·0 | ·0864 | ·0163 | 0·233 | ·000 | 10·1 | ·776 |
| 21 | 85 | 2·0 | ·0432 | ·0202 | ·116 | ·000 | 19·0 | ·75 |
| 22 | 85 | 2·0 | ·0214 | ·0201 | ·0582 | ·000 | 36·1 | ·72 |
| | | | *Order with respect to* $CoY^{-1}$ | | | | | |
| 50 | 85 | 2·0 | ·0402 | ·0194 | ·000 | ·0030 | 17·8 | ·65 |
| 51 | 85 | 2·0 | ·0402 | ·0389 | ·000 | ·0030 | 12·9 | ·68 |
| 53 | 85 | 2·0 | ·0402 | ·0583 | ·000 | ·0030 | 10·1 | ·70 |
| 58 | 85 | 2·0 | ·0s02 | ·0875 | ·000 | ·0030 | 7·7 | ·71 |
| 59 | 85 | 2·0 | ·0402 | ·117 | ·000 | ·0030 | 5·5 | ·80 |
| | | | *pH dependence* | | | | | |
| 61 | 85 | 1·00 | ·0402 | ·0292 | ·000 | ·0030 | | ·00 |
| 62 | 85 | 2·87 | ·0402 | ·0292 | ·000 | ·0030 | 18·0 | ·56 |
| 63 | 85 | 3·68 | .0402 | ·0292 | ·000 | ·0030 | 23·1 | ·43 |
| 64 | 85 | 4·99 | ·0402 | ·0355 | ·000 | ·0030 | 29·0 | ·32 |
| | | | *Exchange between* $Co^{+2}$ *and* $CoY^{-1}$ | | | | | |
| 49 | 85 | 2·0 | ·000 | ·0292 | ·0402 | ·000 | ∞ | |
| | | | *Temperature dependence* | | | | | |
| 54 | 70 | 2·0 | ·0402 | ·0194 | ·000 | ·0030 | 56·5 | ·21 |
| 55 | 70 | 2·0 | ·0402 | ·0292 | ·000 | ·0030 | 48·8 | ·21 |
| 56 | 60 | 2·0 | ·0402 | ·0194 | ·000 | ·0030 | 162 | ·072 |
| 57 | 60 | 2·0 | ·0402 | ·0292 | ·000 | ·0030 | 130 | ·077 |

[a] For runs at an initial $p$H of 2·0, the average $p$H was some what higher because of a drift upwards of a few tenths of a $p$H unit during the course of a run. [b] These are essentially formalities; they are computed on the basis of an infinite stability constant for $CoY^{-2}$. The quantity $Y$ denotes the formality of unbound ligand. For the runs at $p$H 2, with zero excess $Co^{+2}$, the actual concentrations of $CoY^{-2}$ were five to ten per cent lower than the formalities, and the true values for $k_{2nd}$ should be correspondingly higher than those given.

The quantities $a'$ and $a$ were generally the same, except for runs 19 through 22, which contained excess $Co^{+2}$ ion. In the remaining runs, excess cobaltous nitrate was added just before separation, and the appropriate correction for this dilution was applied to the measured specific activity of the cobaltous fraction.

Some decomposition occurred during the course of the exchange runs, as evidenced by a rise in $p$H of several tenths of a unit; however, as shown by run 49, this did not result in any appreciable amount of Co(II) being formed. In addition, runs not reported in the table indicated some surface catalysis in that a two-thousandfold increase in amount of glass surface led to a sixfold increase in rate. Also, while ordinary laboratory lighting had no effect, some photoinduced exchange was observed with a high-intensity mercury source. Finally, increasing the ionic strength from 0·2 to 0·7 by the addition of barium chloride increased $R$ by about ten per cent.



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The second-order specific rate constants are reasonably constant, and the average value at 85°C and *p*H 2·0 is taken to be $0{\cdot}75 M^{-1}\ hr^{-1}$. With respect to the effect of *p*H on the apparent second-order rate constant, the exchange was slow at *p*H 1 undoubtedly because at this *p*H very little Co(II) existed in the form of $CoY^{-2}$. The reduction in rate at *p*H values greater than 2 cannot be explained on this basis but the effect was not large and a detailed study was not made of this effect.

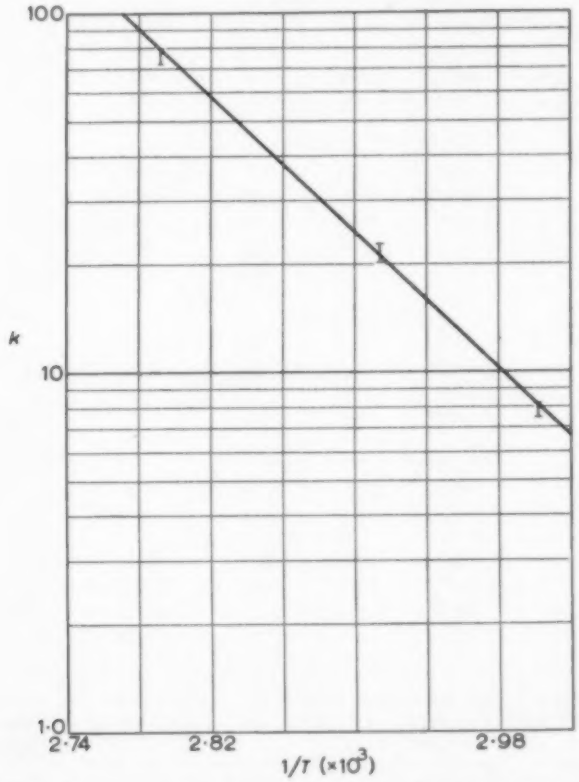


FIG. 2.—Temperature dependence of the exchange between $CoY^{-2}$ and $CoY^{-1}$.

The temperature dependence data are shown in Fig. 2, and lead to an activation energy of 22 kcal/mole and, at 85°C, to an entropy of activation of −17 cal/deg.mole.

## DISCUSSION

It seems reasonable to suppose that the observed second-order kinetics for the cobalt system corresponds to the process

$$CoY^{-2} + Co\,Y^{-1} = CoY^{-1} + Co\,Y^{-2} \qquad (2)$$

and similarly for the iron system. The alternative scheme,

$$\begin{aligned} 2H^{+} + CoY^{-2} &= Co^{+2} + H_2Y^{-2} \\ 2H^{+} + CoY^{-1} &= Co^{+3} + H_2Y^{-2} \\ Co^{+2} + Co^{+3} &= Co^{+3} + Co^{+2} \quad \text{(slow)} \end{aligned} \qquad (3)$$

may be ruled out on various grounds, but especially in view of the fact that negligible exchange occurred between $Co^{-2}$ and $CoY^{-1}$ (run 49) and that the rate constant did not depend upon whether Co(II) or Y was in excess. This, moreover, is consistent with the report that the exchange between $Co^{+3}$ and $CoY^{-1}$ is very slow.[15] Similarly, because of the slow exchange between $Fe^{+3}$ and $FeY^{-1}$,[12] it again seems reasonable to suppose that the rapid exchange between $FeY^{-2}$ and $FeY^{-1}$ occurs by a charge transfer path of type (2).

The species $[Co(Y)(H_2O)]^{-1}$ has been reported by SCHWARZENBACH,[11] in which the water appears to occupy a co-ordinate position. In acid solution, however, this species is unstable with respect to the normal form $CoY^{-1}$ employed here. There is a possibility, however, that the Co(II) complex exists to some extent in the form $[Co(Y)(H_2O)]^{-2}$, since information on this point is lacking.

The great difference in charge transfer lability of the two systems studied here must seemingly be attributed mainly to differences in the nature of the electronic states of the iron and cobalt central metal ions; valence states, net charges, and the nature of the co-ordination sphere are all similar. Moreover, in examining the data available on iron and cobalt systems, as collected in Table 2, it now seems significant that charge transfer in general is rapid with the iron systems and slow with the cobalt ones.

TABLE 2.—CHARGE TRANSFER RATES FOR IRON AND COBALT SYSTEMS

| System | Rate or $k_{2nd}$ | $\Delta H$ (kcal) | $\Delta S$ (cal/°) | $I_i$ | $\Delta I$ | References[a] |
|---|---|---|---|---|---|---|
| $Fe(CN)_6^{-4}$—$Fe(CN)_6^{-3}$ | $k_{50°} = 10^3$ sec$^{-1}$ | | | 1 | 0 | 4 |
| $FeP_3^{+2}$—$FeP_3^{+3}$[b] | imm. fast | | | 1? | 0? | 22 |
| $FeY^{-2}$—$FeY^{-1}$ | imm. fast | | | 9 | 0 | 23 |
| $Fe^{+2}$—$Fe^{+3}$ | $k_{0°} = \cdot 87$ sec$^{-1}$ | 10 | −25 | 9 | 0 | 24, 7 |
| $Co^{+2}$—$Co^{+3}$ | imm. fast | | | 3 | 2 | 20, 25 |
| $Co(C_2O_4)_3^{-4,-3}$ | $k_{50°} = 3$ hr$^{-1}$ | | | 3 | 2 | 26 |
| $Co(NH_3)_6^{+2,+3}$ | $k_{45°} = \cdot 002$ hr$^{-1}$ | | | 3 | 2 | 27 |
| $Co(en)_3^{+2}$—$Co(en)_3^{+3}$ | $k_{25°} = \cdot 18$ hr$^{-1}$ | 14 | −33 | 3 | 2 | 27 |
| $CoY^{-2}$—$CoY^{-1}$ | $k_{85°} = \cdot 75$ hr$^{-1}$ | 22 | −17 | 3 | 2 | 23 |

[a] Susceptibilities, if not in the articles referred to, are taken from P. W. SELWOOD, *Magnetochemistry*, Interscience Publisher, Inc., New York, N.Y. (1943).
[b] P denotes 5,6 dimethyl-1,10 phenanthroline.

In terms of the crystal-field theory for the energy levels for transition metal ions,[17, 18, 19] the species in Table 2 may be classified as having strong or weak ligand fields, as indicated by the magnetic susceptibility being normal or anomalous. It is seen that in the case of the iron systems no change in type occurs, whereas for the cobalt ones exchange occurs between Co(II)(weak field) and Co(III)(strong field). The apparent exception, $Co^{+2}$—$Co^{+3}$, can be accounted for if one adapts the suggestion[20] that for $Co^{+3}$ the paramagnetic state is sufficiently low lying to be

[17] J. BJERRUM, C. J. BALLHAUSEN, and K. JØRGENSEN *Acta. Chem. Scand.* **8**, 1275 (1954), and subsequent papers.
[18] L.E. ORGEL *J. Chem. Phys.* **23**, 1004 (1935).
[19] H. HARTMANN *Z. physik. Chem.* **4**, 376 (1955).
[20] H. L. FRIEDMAN, J. P. HUNT, R. A. PLANE, and H. TAUBE *J. Amer. Chem. Soc.* **73**, 4028 (1951).

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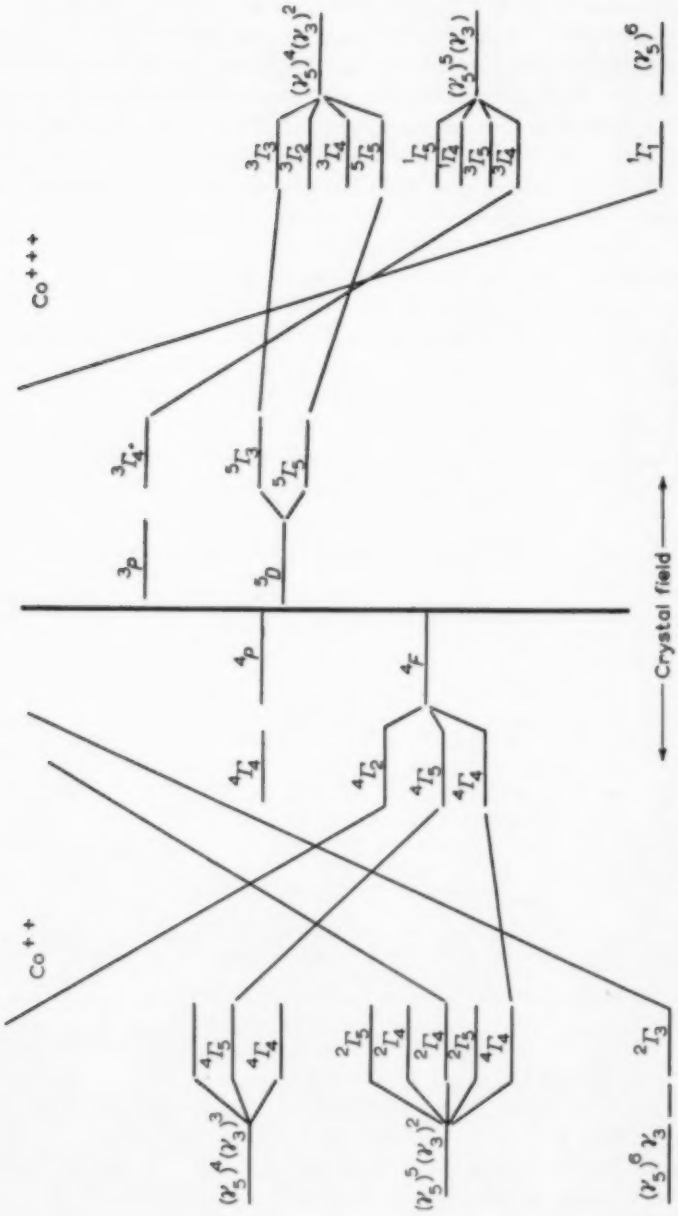


FIG. 3.—Crystal-field energy-level diagram for $Co^{++}$ and $Co^{+++}$.

thermally accessible. As an empirical observation, it has been noted that charge transfer labilities may be predicted qualitatively by means of a simple function of the magnetic susceptibilities (or equivalent number of unpaired electrons) of the two ions.[1]

A qualitative explanation of the slowness of the charge transfer with cobalt systems can be given in terms of the crystal-field energy-level diagrams for Co(II) and Co(III) as shown in Fig. 3.[21] Since the Franck Condon principle applies to the charge transfer act, metal-to-ligand distances, and, to an approximation, the field due to the ligands, should be invariant. A charge transfer between normal ions would then correspond to the process

$$\text{Co(II)(weak field, 3)} + \text{Co(III)(strong field, 0)}$$
$$= \text{Co(III)(weak field, 4)} + \text{Co(II)(strong field, 1)} \qquad (4)$$

where the numbers indicate the number of unpaired electrons; thus $I_i = 3$ and $\Delta I = 2$, where $I_i$ denotes the units of angular momentum for the reaction complex before charge transfer, and $\Delta I$, the change upon charge transfer. In terms of the crystal-field energy diagram, process (4) should be quite endoergic. Since the charge-transfer act is adiabatic, this energy requirement presumably must be supplied as an energy of activation for the reactants. In addition, process (4) calls for a change in multiplicity of the reaction complex, and there should be a reduced probability for the electronic change which would be reflected as a negative entropy of activation. This last effect would not be present, however, with highly activated reactants:

$$\text{Co(II)(strong field)} + \text{Co (III)(weak field)}$$
$$= \text{Co(III)(strong field)} + \text{Co(II)(weak field)} \qquad (5)$$

The average reaction path would be the optimum compromise between (4) and (5).

The above source of activation energy and entropy would be minimal for the iron systems for which the process analagous to (4) would not involve ions having greatly different crystal field parameters. Data are available for several systems of the type $Fe^{+2}$—$FeX^{+2}$, where X may be $OH^-$, $Cl^-$, or $F^-$. While not of the "pure" charge transfer type because of the differing stoichiometry, the fact the exchange rates are all similar and close to that for $Fe^{+2}$—$Fe^{+3}$ has been noted as indicating that a common rate determining step is involved.[24, 28]. This conclusion is strengthened by the finding that the exchange rates for $Fe^{+2}$—$Fe^{+3}$ and $Fe^{+2}$—$Fe(OH)^{+2}$ are reduced by the same factor in heavy water as a solvent.[24] It is suggested here that this common rate controlling factor is the nature of the crystal-field energy levels for the two species.

The data in Table 2, as well as that for charge transfer systems involving other central metal ions, indicate that an order of magnitude classification of rates can be

[21] This qualitative representation was kindly supplied by C. J. BALLHAUSEN.
[23] L. EIMER and A. I. MEDALIA *J. Amer. Chem. Soc.* **74**, 1592 (1952).
[23] Susceptibility of $NH_4FeY \cdot H_2O$ and KCoY given by W. KLEMM *Z. anorg. Chem.* **252**, 225 (1944).
[24] J. HUDIS and R. W. DODSON *J. Amer. Chem. Soc.* **78**, 911 (1956).
[25] S. A. HOSHOWSKY, O. G. HOLMES, and K. J. MCCALLUM *Canad. J. Res.* **27B**, 258 (1948).
[26] A. W. ADAMSON, H. OGATA, J. GROSSMAN, and R. NEWBURY, April, 1956 meeting of the American Chemical Society, Dallas, Texas.
[27] W. B. LEWIS, C. D. CORYELL, and J. W. IRVINE JR. *J. Chem. Soc.* S386 (1949).
[28] J. HUDIS and A. C. WAHL *J. Amer. Chem. Soc.* **75**, 4153 (1953).

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made in terms of $I_i$ and $\Delta I$ values. There are still considerable variations within each group, as would be expected from crystal-field considerations alone since the degree of splitting of the 3*d* orbitals varies from one ligand to another. However, as WILLIAMS[29] points out, a detailed theory of crystal-field energetics requires a molecular orbital approach, and an accurate treatment becomes complicated.

*Acknowledgements*—This investigation was supported in part by a contract between the University of Southern California and the US Office of Naval Research.

[29] R. J. P. WILLIAMS *J. Chem. Soc.* **8**, (1956).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 215 to 228. Pergamon Press Ltd., London

# INTERRELATIONSHIPS IN THE SOLVENT EXTRACTION BEHAVIOUR OF SCANDIUM, THORIUM, AND ZIRCONIUM IN CERTAIN TRIBUTYL PHOSPHATE-MINERAL ACID SYSTEMS*

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**Abstract**—The extraction behaviour of Sc and that of Th in the aqueous HCl-TBP (tributyl phosphate) system differ sufficiently that these elements are readily separable. Although the respective extraction curves tend to converge as the HCl concentration is lowered, they do not intersect. In contrast, the Sc and Th extraction curves in the $HNO_3$-TBP systems mutually cross.

The complete Zr extraction curves have not been determined, but the Zr extraction curve in the $HNO_3$-TBP system is shown to cross both the Sc and Th curves. Consequently, in this system, any one of the three elements may be separated as product from the other two as contaminants.

In the HCl-TBP system, the TBP dependency of the extraction coefficients for Sc and Th are not readily interpretable. In the $HNO_3$-TBP system the TBP dependencies are operationally fourth-power at high $HNO_3$ concentrations and considerably less than fourth-power at intermediate and low $HNO_3$ concentrations.

The mutual separation of a Th-Sc mixture and of a Th-Zr mixture in the HCl-TBP system and the isolation of each of the three elements as product from a Sc-Th-Zr mixture in the $HNO_3$-TBP system are demonstrated.

## INTRODUCTION

FROM the commonly applied generalization that the first member of a periodic group should resemble, rather closely, the second member of the next higher group, a pronounced similarity in the behaviour of Sc(III) and Zr(IV) is to be expected. However, from an abundance of data in the literature, it is evident that the mutual separation of these elements may be effected easily by a number of precipitation techniques. In contrast, the mutual separation of Sc(III) and Th(IV) by precipitation techniques is exceedingly difficult.

On the other hand, a liquid–liquid extraction technique involving the extraction of scandium thiocyanate into diethyl ether permits the ready mutual separation of Sc and Th;[1] but the Sc is accompanied by any Zr present, as shown by experiments performed in this laboratory.

The observation of this complexity in the relative behaviour of these three elements initiated an extension of studies reported in fragmentary fashion elsewhere—namely the extraction of scandium[2] into tri *n*-butyl phosphate, symbolized by TBP, from

* Based on work performed under the auspices of the US Atomic Energy Commission.

[1] W. FISCHER and R. BOCK *Z. anorg. allgem. Chem.* **249**, 146 (1942).

[2] (a) D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. Phys. Chem* **57**, 294 (1953) report the separation of macro scandium from macro yttrium, rare earths, etc. by use of a TBP-HCl system, and present $Sc^{46}$ tracer data for distribution ratios in this system. The data for 3·0M and for 6·4M HCl are seen to be in error (cf. Fig. 1, this paper), presumably due to the presence of traces of pyrophosphate esters in the TBP. (b) A. R. EBERLE and M. W. LERNER *Analyt. Chem.* **27**, 1551 (1955) report the extraction of scandium into TBP from HCl; but their $Sc^{46}$ tracer data are for TBP as received, and the solvent was not pre-equilibrated with respect to HCl. They did not use the TBP-HCl system for effecting a Sc-Th separation.

HCl and from $HNO_3$, and the extraction of thorium[3, 4] into TBP from $HNO_3$—to include comparable data for the three elements in both TBP-HCl and TBP-$HNO_3$ systems.

The batch data, so obtained, were applied in a series of discontinuous, countercurrent experiments in which the relative distributions of scandium, thorium and zirconium between an aqueous phase containing nitric or hydrochloric acid and an organic phase containing TBP were utilized to effect the mutual separation of these three elements.

*Pertinent Mathematics of Discontinuous Countercurrent Extraction*

Consistent with the usuage of PEPPARD *et al.*[2, 5] it is assumed that a solute is distributed at equilibrium between two immiscible liquid phases (of different densities) and that the separate portions of these phases move countercurrently with respect to each other in a discontinuous fashion, feed being introduced at each cycle.

If the assumption is made that the ratio of the quantity of the given solute in the upper phase to that in the lower phase in a given stage is $U$ in the "scrub section", $E$ in the "extraction section" and $P$ in the "feed entry stage", then from material balance considerations it is readily seen[5] that:

$$F = PU^{n-1}\sum_{i=0}^{q-n} E^i \Big/ \left[\sum_{i=0}^{n-1} U^i + PU^{n-1}\sum_{i=0}^{q-n} E^i\right] \tag{1}$$

$$\phi = \sum_{i=0}^{n-1} U^i \Big/ \left[\sum_{i=0}^{n-1} U^i + PU^{n-1}\sum_{i=0}^{q-n} E^i\right] \tag{2}$$

where, referred to the quantity of solute in a single portion of feed, $F$ and $\phi$ are the respective fractions of solute reporting in single fractions of upper and lower phases effluent from the system at steady state, and $U$, $E$, and $P$ are constants for a given system.

In the terminology used above, the scrub (barren lower phase) is introduced at the first contactor, the feed (any form) is introduced at the $n$th contactor and the solvent (barren upper phase) is introduced at the $q$th (final) contactor. The pregnant upper and lower phases are removed from the system at the first and $q$th stages respectively. Therefore, contactors 1 to $(n-1)$ inclusive, and contactors $(n+1)$ to $q$ inclusive, respectively constitute the scrub and extraction sections.

From symmetry considerations the case of $q = 2n - 1$, to which the remainder of this treatment will be restricted, is of special interest. Introducing the concept of decontamination factor $DF$ defined (in this paper), for the product $A$, as the ratio of $A$ to $B$ in the product divided by the ratio of $A$ to $B$ in the feed, it may be shown from equations (1) and (2) that for this case:

$$(DF_{A/B})_{\text{Upper phase}} = (DF_{B/A})_{\text{Lower phase}}$$

if $E_A = 1/U_B$, $U_A = 1/E_B$ and $P_A = 1/P_B$. (These conditions reduce to $E_A = 1/E_B$, if $E = U = P$ for each of the solutes, as shown by BUSH and DENSEN.[6]) The

[3] D. F. PEPPARD, G. ASANOVICH, R. W. ATTEBERRY, O. DUTEMPLE, M. V. GERGEL, A. W. GNAEDINGER, G. W. MASON, V. H. MESCHKE, E. S. NACHTMAN, and I. O. WINSCH *J. Amer. Chem. Soc.* **75**, 4576 (1953).
[4] D. F. PEPPARD, M. H. STUDIER, M. V. GERGEL, G. W. MASON, J. C. SULLIVAN, and J. F. MECH *J. Amer. Chem. Soc.* **73**, 2529 (1951).
[5] D. F. PEPPARD and M. A. PEPPARD *Ind. Eng. Chem.* **46**, 34 (1954).
[6] M. T. BUSH and P. M. DENSEN *Analyt. Chem.* **20**, 121 (1948).

expression for the $DF$ (for equal degree of mutual separation) is readily shown to be:

$$DF = \sum_{i=0}^{1-n} U_B^i \Big/ P_B \sum_{i=0}^{n-1} E_B^i \tag{3}$$

For the special case of $E_A = \beta E_B$, $U_A = \beta U_B$, $P_A = \beta P_B$ and $q = 2n - 1$, equation (3) reduces to:

$$DF = \beta^{0.5} \sum_{i=0}^{n-1} (\beta E_B)^i \Big/ \sum_{i=0}^{n-1} E_B^i \tag{4}$$

As $E_B$ increases without limit, this function approaches the limiting value:

$$DF = \beta^{n-0.5}, \qquad (\text{For } E_B \to \infty). \tag{5}$$

This value is to be compared with the value:

$$DF = \beta^{0.5n}, \qquad (\text{For } E_B = U_B = P_B) \tag{6}$$

which is obtained from equation (3) by setting $E_B = U_B = P_B$.

It is, therefore, obvious that the maximum degree of mutual separation is not obtained by setting $E_B = U_B = P_B$ (and $E_B = 1/E_A$) but by arranging to have the $E$ values as large as possible, the $U$ values as small as possible and the $P$ values equal to $\beta^{0.5}$ and $\beta^{-0.5}$, respectively. For ideal systems, assuming feed introduction into the lower phase, this set of conditions may be obtained only if, for a given solute, the $K$ value in the scrub section is smaller than that in the extraction section, since the volume ratio of upper to lower phase is necessarily larger in the scrub section than in the extraction section. (In this paper, the distribution ratio, $K$, for a given solute, is defined as the ratio of the concentration in the upper phase to that in the lower phase, the concentrations being expressed in terms of unit volume.) For ideal systems, the constant $\beta$ is the ratio of $K_A$ to $K_B$.

For nearly ideal systems in which, for each solute, $K$ is sensibly constant throughout and the feed is introduced in a volume negligible with respect to the volume of scrub (or in which the $K$'s are so adjusted that the product of $K$ and the volume ratio is a constant), equations (1) and (2), for $q = 2n - 1$, reduce respectively to SCHEIBEL's[7] expressions:

$$F = E^n/(1 + E^n) \tag{7}$$

$$\phi = 1/(1 + E^n) \tag{8}$$

for which equation (6) gives the $DF$ for equal degree of mutual separation. Using equations (7) and (8) and the relation $E_A = \beta E_B$, it may be shown that for the case of nonequal degree of mutual separation:

$$DF = \beta^n(1 - Y) + Y, \qquad (\text{For } q = 2n - 1, E = U = P.) \tag{9}$$

where $Y$ is the fractional yield of the product solute.

From equation (9) it is seen that to a very close approximation the $DF$ increases linearly with the fractional loss of the product solute: so that, for example, a given system may be operated to produce a product, of given contaminant content, in

[7] E. G. SCHEIBEL *Ind. Eng. Chem.* **43**, 242 (1951).

99·00% yield or a product, containing 100 times more contaminant, in 99·99% yield. Consequently, if, of the solutes present, only one is considered a product, it is usually advantageous to sacrifice some yield in the interest of purity.

In deciding whether, in the case of equal degree of mutual separation, to strive for a *DF* of which equation (5) gives the limiting value or to settle for the *DF* of equation (6), it is instructive to consider both the effect of holdup and the number of cycles required to approximate steady-state operation. It may be seen, by reference to the analysis by PEPPARD and PEPPARD,[5] that operation with large *E*'s and small *U*'s intensifies both of these problems. However, in working with micro-level concentrations of solutes, *DF* values far in excess of those given by equation (6) have been obtained in this laboratory.

## EXPERIMENTAL

*General.* TBP, as received from Commercial Solvents Corporation, and an equal volume of 8M aqueous HCl were kept intimately agitated at 40 to 50°C for 8 hours for the purpose of hydrolysing any organic pyrophosphates present to a form removable by aqueous alkali. The separated TBP phase was then washed with two one-fifth volume portions of water followed by two one-fifth volume portions of 5% aqueous sodium carbonate followed by two one-fifth volume portions of water. The resulting product, "washed TBP", is free from organic pyrophosphates and from mono- and dibutyl phosphoric acids, all of which have extraction characteristics strikingly different from those of TBP.[3] The diluent, thiophene-free benzene (Merck and Co.) was used as received. In all experiments, washed TBP, or washed TBP plus diluent, was pre-equilibrated with respect to an aqueous phase identical to that under study except that it contained none of the element whose extraction was being investigated. The term, "concentration of TBP" is used to signify the molarity of TBP, or its per cent by volume concentration, in the pre-equilibrated upper phase before introduction of metal ion solute.

Beta-active 85-d $Sc^{46}$, obtained from the Isotopes Division, Oak Ridge National Laboratory, was repurified by the thenoyl trifluoracetone technique of BROIDO.[6] Alpha-active $8{\cdot}05 \times 10^4$ y $Th^{230}$, isolated from Belgian Congo pitchblende-concentrate[3] and with a $Th^{232}$:$Th^{230}$ ratio of approximately 8, was obtained from the Argonne National Laboratory's stocks. The zirconium oxide, used in preparing the chloride and nitrate, had a Hf : Zr mole ratio of less than 0·002.

Unless otherwise indicated, all data were obtained at 22 ± 2°C.

*Determination of K.* The distribution ratio, *K* (concentration in the upper phase divided by concentration in the lower phase), was determined for radioactive species as in previous studies in the series.[3, 9]

The *K* values for zirconium were obtained by equilibrating an aqueous nitric or hyrochloric acid phase containing zirconium in gross concentration with a solvent phase, equilibrating the separated solvent phase successively with two portions of aqueous scrubs of the proper composition (pre-equilibrated with respect to barren solvent phase), and analysing suitable aliquots of the two scrubs and the final scrubbed solvent. The *K* values for the first and second scrubbing were computed and found to be in agreement.

In order to ensure the extractability of Zr, the proper zirconium salt (chloride or nitrate) was heated under reflux in the corresponding mineral acid, which was at least 6*M*, for a period of at least 8 hours. This solution was cooled and converted to feed for immediate use.

For determinations of *K* less than unity, the volume ratio of scrub to solvent was 0·20. For determinations of *K* greater than unity, this volume ratio was increased. For example, in the determination of *K* approximately equal to 1000, this ratio was 25 (80 ml of solvent, 2000 ml of scrub).

The zirconium content of the solvent phase was returned to an aqueous phase by equilibrating the solvent with four equal-volume portions of water.

Residual traces of solvent were removed from the combined aqueous re-extract by agitating this phase with benzene. Traces of solvent were removed from the aqueous scrubs in the same manner.

[6] A. BROIDO *U.S. Atomic Energy Commission Declassified Document AECD*-2616, July 29, 1947.
[9] D. F. PEPPARD, P. R. GRAY, and M. M. MARKUS *J. Amer. Chem. Soc.* **75**, 6063 (1953).

Suitable portions of the TBP-free aqueous re-extract and scrubs were evaporated to approximately 50-ml portions in glass beakers, and these concentrates were then evaporated, in portions, in platinum crucibles of approximately 30-ml capacity.

Following evaporation to dryness, the samples were ignited to oxide in a muffle furnace by slowly raising the temperature of the furnace from room temperature to 850°C and holding the furnace at this temperature for two hours. The weighed oxides were then dissolved by prolonged heating with

TABLE 1.— DISCONTINUOUS COUNTERCURRENT FRACTIONATION OF Th FROM Sc AND Zr BY USE OF HCl-100% TBP[11] SYSTEMS*

(Seven-stage, centre-feed, i.e. $q = 7$, $n = 4$.)

| Run no. | MHCl scrub | $R$ | $G$ | $C$ (component) | M of $C$ feed | % $C$ found in phase | | % $C$ (theoretical†) in phase | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Upper | Lower | Upper | Lower |
| 1 | 7·0 | 1·00 | 1·33 | Th | 0·1 | <0·1 | 100 | 0·01 | 100 |
| | | | | Sc | 0·5 | 100 | <0·01 | 100 | $3 \times 10^{-3}$ |
| | | | | Zr | 0·01 | <99 | <1 | 100 | $6 - 10^{-4}$ |
| | | | | HCl | 7·0 | — | — | — | — |
| 2 | 7·0 | 0·80 | 1·07 | Th‡ | 0·05 | $4 \times 10^{-3}$ | 100 | $5 \times 10^{-3}$ | 100 |
| | | | | Sc | 0·4 | 100 | 0·01 | 100 | $6 \times 10^{-2}$ |
| | | | | Zr | 0·1 | 100 | <0·5 | 100 | $1 \times 10^{-5}$ |
| | | | | HCl | 7·0 | — | — | — | — |
| 3 | 7·0 | 0·222 | 0·250 | Th‡ | 0·5 | $3 \times 10^{-5}$ | 100 | $2 \times 10^{-6}$ | 100 |
| | | | | Sc | 0·2 | 98 | 2 | 99·0 | 1·0 |
| | | | | Zr | 0·02 | >98 | <2 | 100 | $2 \times 10^{-3}$ |
| | | | | HCl | 7·0 | — | — | — | — |
| 4 | 7·0 | 3·00 | 3·75 | Th‡ | $5 \times 10^{-4}$ | 0·4 | 99·6 | 0·7 | 99·3 |
| | | | | Sc | 0·2 | 100 | $<8 \times 10^{-5}$ | 100 | $3 \times 10^{-5}$ |
| | | | | Zr | 0·2 | 100 | $<2 \times 10^{-4}$ | 100 | $7 \times 10^{-5}$ |
| | | | | HCl | 7·0 | — | — | — | — |

* The pre-equilibrated solvent phase is approximately 3M in TBP.

† Equations (1′) and (2′) and the data of Fig. 1, neglecting the effect of bound TBP, were used in the theoretical treatment.

‡ The Th was a freshly-purified $Th^{230}/Th^{232}$ mixture with a mass ratio of 0·1. The Th assay was by alpha counting.

hydrochloric acid containing a small quantity of hydrofluoric acid. Spectrographic examination of these dissolved samples showed negligible quantities of contaminants.

In each determination a quantity of solvent (or aqueous scrub) sufficient to yield at least 100 mg of ignited oxide was analysed. After a ten-minute settling period the phases were separated by means of a separatory funnel, the fractions near the interface being discarded. The separated phases were then allowed to stand overnight for further settling. In the determination of extremely large $K$'s, the aqueous phase was finally centrifuged. It is believed that these precautions made all errors other than those involved in the actual analyses negligible.

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TABLE 2.— DISCONTINUOUS COUNTERCURRENT FRACTIONATION OF Th, Sc, AND Zr, BY USE OF $HNO_3$-TBP SYSTEMS

(Seven-stage, centre-feed, i.e. $q = 7$, $n = 4$.)

| Run no. | % TBP[11] solvent | M $HNO_3$ scrub | $R$ | $G$ | $C$ (component) | M of $C$ feed | % $C$ found | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Upper | Lower |
| 1 | 100 | 1·96 | 0·43 | 0·50 | Th | 0·45 | 100 | <0·1 |
| | | | | | Sc | 0·45 | 0·4 | 100 |
| | | | | | Zr | 0·45 | <0·1 | 100 |
| | | | | | $HNO_3$ | 2·0 | — | — |
| 2 | 50 | 6·07 | 0·60 | 0·75 | Th | 0·11 | 100 | <0·1 |
| | | | | | Sc | 0·11 | 0·02 | 100 |
| | | | | | Zr | 0·11 | 100 | <0·1 |
| | | | | | $HNO_3$ | 6·0 | — | — |
| 1 | 20 | 11·9 | 0·50 | 0·60 | Th | 0·09 | <0·1 | 1·00 |
| | | | | | Sc | 0·09 | 0·02 | 100 |
| | | | | | Zr | 0·09 | 100 | <0·1 |
| | | | | | $HNO_3$ | 12 | — | — |

*Discontinuous Countercurrent Extraction.* The double-diamond method of operation previously used by PEPPARD *et al.*[3] and referred to as pseudo countercurrent extraction by HUNTER and NASH[10] was used, the feed being introduced at the centre stage and the extractant and scrub at the terminal stages of a seven-stage assembly of 125-ml contactors. Contact and settling times of three and two minutes respectively were used. Agitation was by means of motor-driven stirrers, and transfers were made manually, the lower and upper phases respectively of the $(p - 1)$th and $(p + 1)$th stages being drained to a common beaker whose contents were then poured into the $p$th contactor.

Extractions were continued for a number of cycles at least twice the number calculated, in approximate fashion, to be necessary for attainment of 99% of steady-state operation, using the mathematical treatment of PEPPARD and PEPPARD.[5] As a check, the product phases of both the final cycle and of the fifth-to-last cycle were analysed and found to be in good agreement.

For assay, the metal content of the organic product phase was returned to an aqueous phase by re-extraction into dilute HCl or $HNO_3$, and the aqueous re-extract was washed with Gulf Solvent BT or benzene to remove traces of TBP. The aqueous product phase was washed in the same manner to remove residual TBP.

Aliquots of these re-extracts (and of aqueous product phases) were analysed spectrographically for purity determination.

In certain cases, in order to increase the sensitivity of assay, a product phase was subjected to further extraction before determination of contaminant. For example, by extracting 100 ml of an aqueous Th product, in 7M HCl, with 20 ml of TBP and in turn scrubbing this TBP extract with 100ml of 7M HCl, a TBP extract is obtained which contains 50 ± 20% of the Sc and less than 0·1% of the Th initially present in the portion of Th product.

In each experiment reported in Tables 1 and 2, conditions were so adjusted that approximately 80% or more of the TBP in the upper phase would be free TBP, i.e. TBP not associated directly with the extracted species.

All data of Tables 1 and 2 are reported using the analytical limit which indicates minimum efficiency of separation. It is probable that the separations are more efficient than indicated by the tabular values.

[10] T. G. HUNTER and A. W. NASH *Ind. Eng. Chem.* **27**, 836 (1935) describe a sequence of relative phase movements, designated by them as pseudo countercurrent extraction which, when taken as the batch-analogue of continuous countercurrent extraction, is herein referred to as discontinuous countercurrent extraction.

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## RESULTS

*K Values in TBP-HCl Systems.* The variation of the $K$ values for Sc, Th and Zr with the concentration of HCl in the aqueous phase, using undiluted TBP, is shown in Fig. 1. The $\beta$ value (ratio of $K_A$ to $K_B$) for Sc-Th is seen to be a maximum in the range 7 to 8M HCl in the aqueous phase, with $\beta$ varying only slightly in the range 6 to 9M HCl.

Whether the completed Zr curve would cross either or both of the other curves was not investigated, since it appears certain that the crossing would occur in a region of no interest from a separations viewpoint or would result in a $\beta$ value too small to be of practical importance.

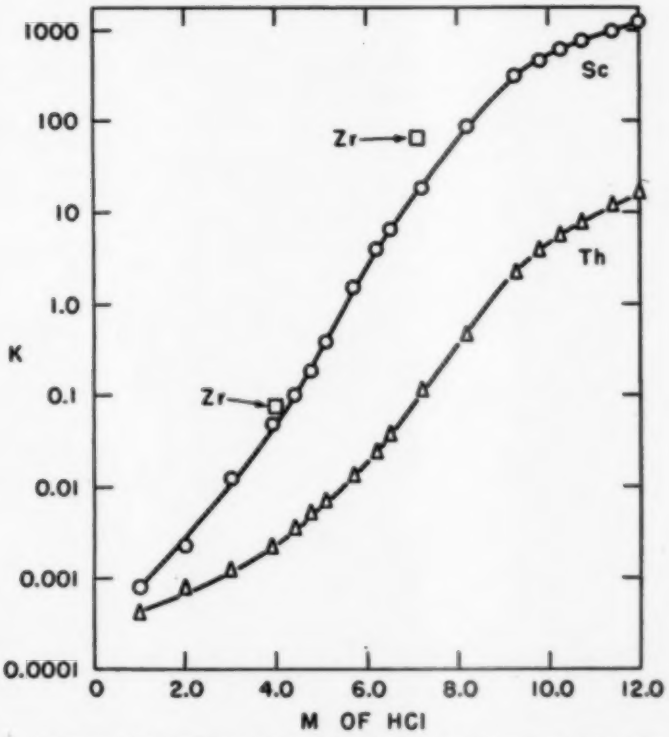


FIG. 1—Variation of distribution ratios of Sc, Th, and Zr with aqueous HCl concentration using 100% TBP.[11] (The approximate TBP concentration varies nearly linearly from 3·4M at 1·0M HCl to 2·8M at 11·4M HCl.)

It is apparent that the mutual separation of Sc and Th and of Zr and Th may be accomplished readily, but the mutual separation of Sc and Zr by use of the HCl-undiluted TBP system is impractical.

The variation of the $K$ values for Sc and Th with the concentration of TBP in the solvent (upper) phase, using two different values of the HCl concentration in the aqueous phase, is shown in Fig. 2. It is evident that no conclusions regarding the composition of the extracting species may be drawn from these fragmentary data.

However, the fact that the $K$ for Sc increases with increasing TBP concentration whereas the $K$ for Th passes through a maximum is of considerable importance from a separations viewpoint, the value of $\beta$ at 100% TBP[11] being 28 times that at 50% TBP[11] with 8·1M HCl as the opposing phase.

*K Values in TBP-$HNO_3$ Systems.* The variation of the $K$ values for Sc, Th, and Zr with the concentration of $HNO_3$ in the aqueous phase, using undiluted TBP, is shown in Fig. 3. It is to be noted that the Sc and Th curves cross each other at approximately 14·6M $HNO_3$ and that the Zr curve (incomplete) crosses each of the

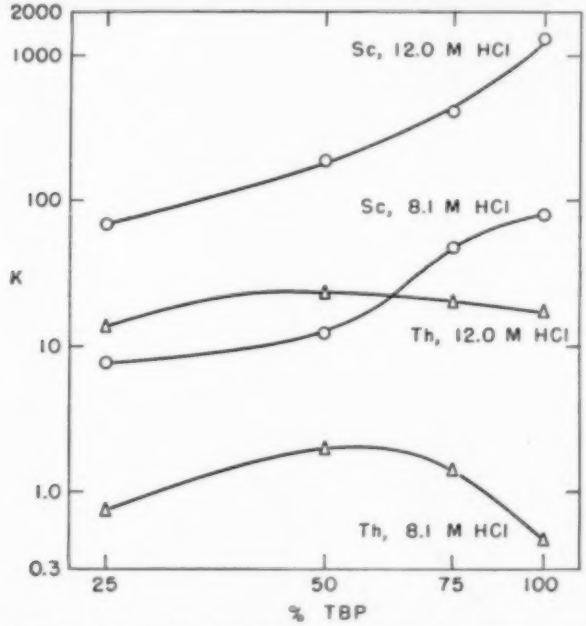


FIG. 2—Variation of distribution ratios of Sc and Th with concentration of TBP in a TBP-benzene solvent using 8·1M HCl and 12·0M HCl as opposing phases.

others at points not accurately determined. As a consequence of these crossings, the $\beta$ values are such that any one of the three elements may, in principle, be separated from the other two.

In practice, certain of these separations are simpler if diluted TBP is used, as shown in Table 2.

The effect of diluting the TBP is shown in Figs. 4 and 5. The lines are drawn with an arbitrary slope of 4 in Fig. 4. It is seen that operationally a fourth-power TBP dependence may be assumed for both Sc and Th at the "high" $HNO_3$ concentrations investigated. Since activities corresponding to these concentrations of TBP are not known, it may only be postulated that the extracting species has a ratio of four TBP molecules per atom of element considered.

[11] The $y$% TBP is a solvent prepared by diluting $y$ volumes of dry TBP to 100 volumes with benzene and pre-equilibrating the resulting solution with respect to the proper aqueous acid solution. The 100% TBP is prepared by pre-equilibrating dry TBP with respect to the proper aqueous acid solution. The molarity of TBP in each of these solvents is dependent upon the concentration of acid in the equilibrated aqueous phase.

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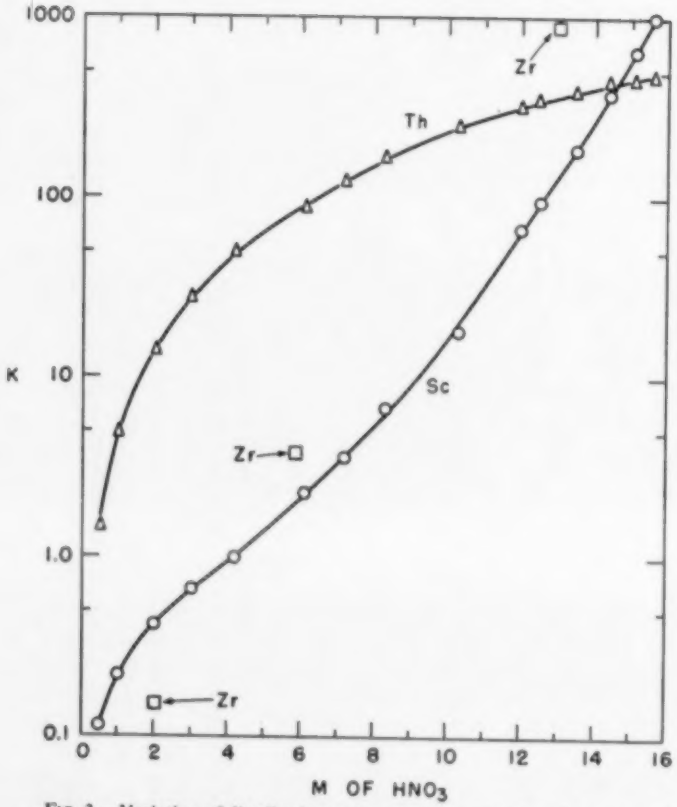


FIG. 3.—Variation of distribution ratios of Sc, Th, and Zr with aqueous $HNO_3$ concentration using 100% TBP.[11] (The approximate TBP concentration varies nearly linearly from 3·5M at 0·5M $HNO_3$ to 2·7M at 16M $HNO_3$.)

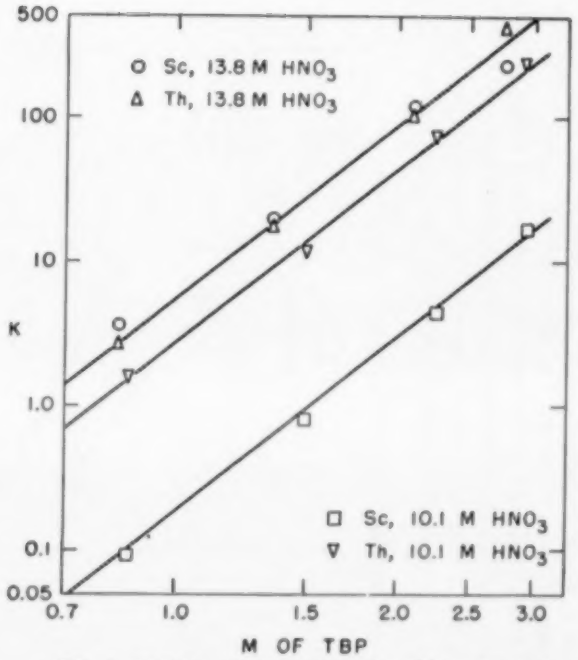


FIG. 4—Variation of distribution ratios of Sc and Th with concentration of TBP in a TBP-benzene solvent using 13·8M $HNO_3$ and 10·1M $HNO_3$ as opposing phase. (Lines drawn with slope 4.)

From Fig. 5 it is evident that departures from operational fourth-power dependencies are extreme at the "low" concentrations of $HNO_3$ investigated.

The large differences between TBP dependencies at high and low $HNO_3$ concentrations indicated that an acid-dependency curve for a $HNO_3$-diluted TBP system should differ considerably from that for a $HNO_3$-undiluted TBP system. The results for a system involving 25% TBP,[11] shown in Fig. 6, are to be compared with those for a system involving 100% TBP,[11] shown in Fig. 3.

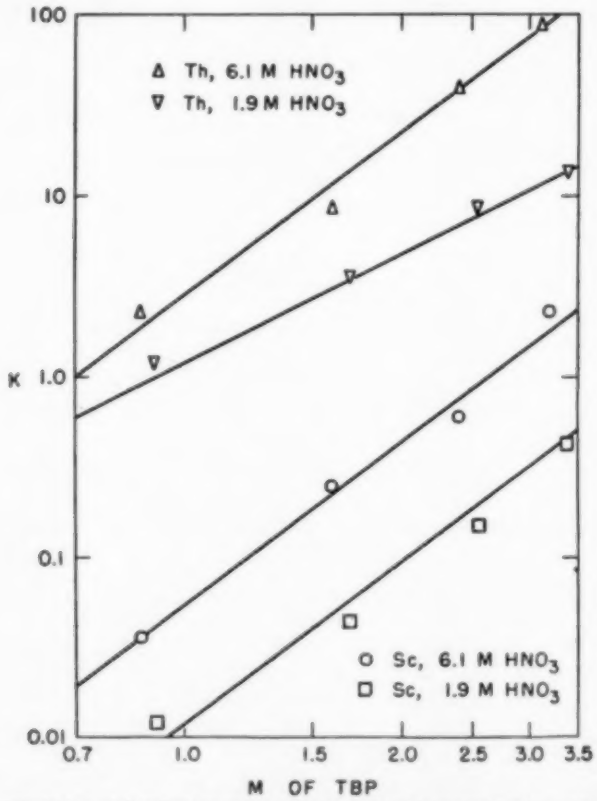


FIG. 5.—Variation of distribution ratios of Sc and Th with concentration of TBP in a TBP-benzene solvent using 6·1M $HNO_3$ and 1·9M $HNO_3$ as opposing phase. (One line drawn with slope 2, others with slope 3.)

Four comparisons of these figures are noteworthy. The Th curve for the 100% system is consistently concave downward, whereas the Th curve for the 25% system displays a maximum followed by a minimum. The general shapes of the two Sc curves are very similar. The Th and Sc curves cross at the more concentrated acid for the more concentrated TBP. The maximum $\beta$ for the 100% system is 50, at 3 to 6M $HNO_3$, whereas that for the 25% system is 80, at 2 to 4M $HNO_3$.

The only accurately-determined Zr point in the 25% system is plotted in Fig. 6. However, approximate values prove the Zr curve to be above that of Th at both 4M $HNO_3$ and 6M $HNO_3$ in this system.

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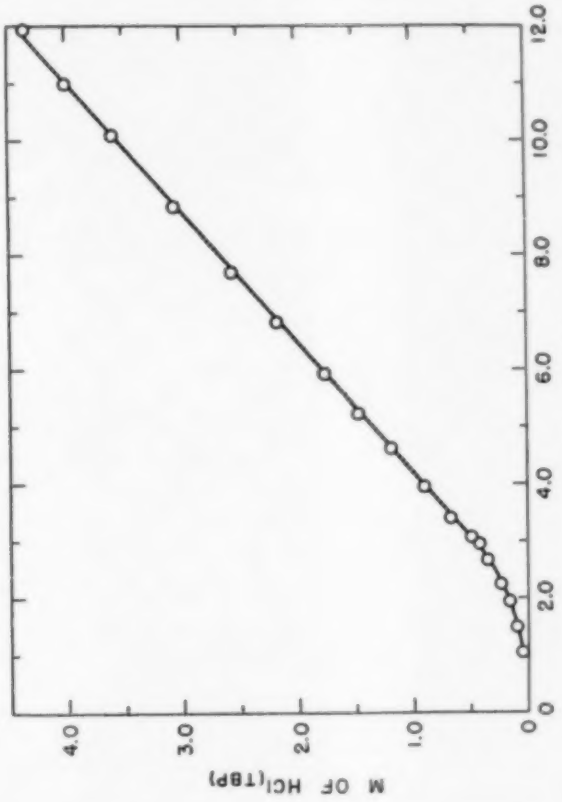


FIG. 7.—Partition of HCl between aqueous and 100% TBP[11] phases at 22 ± 2°C.

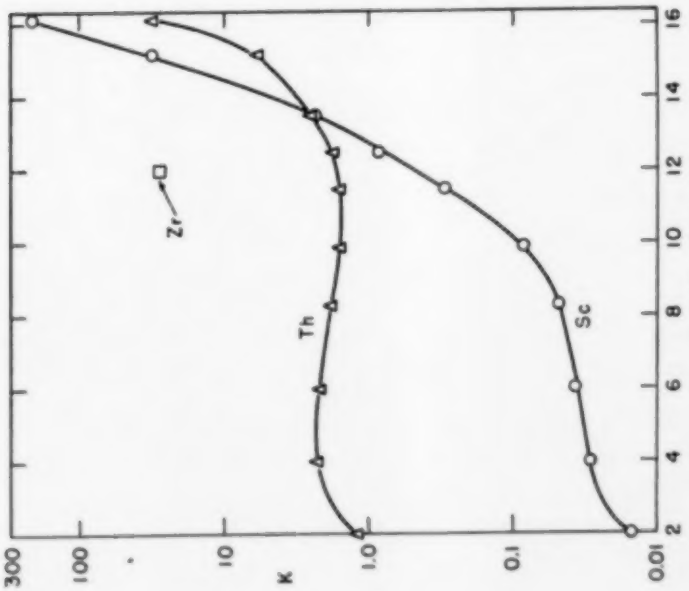


FIG. 6.—Variation of distribution ratios of Sc, Th and Zr with aqueous $HNO_3$ concentration using 25% TBP.[11]

*Partition of Pertinent Mineral Acids.* In the course of pre-equilibration studies the partition of the mineral acids, HCl and $HNO_3$, between an aqueous phase and undiluted TBP was made. The HCl data are shown in Fig. 7. The corresponding $HNO_3$ data are presented in Fig. 8.

*Separation of Sc (and Zr) from Th by use of TBP-HCl Systems.* Following the substitutions $RK = E = P$, $GK = U$, $q = 2n - 1$, equations (1) and (2) were used in the

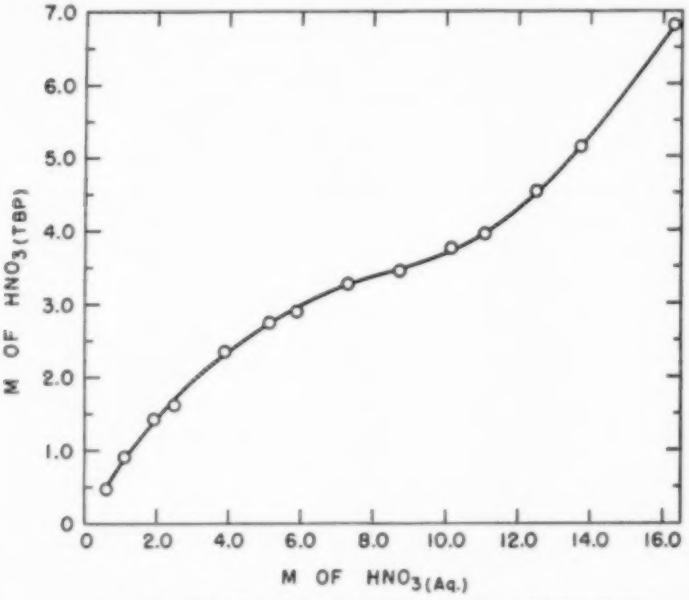


FIG. 8.—Partition of $HNO_3$ between aqueous and 100% TBP[11] phases at 22 ± 2°C.

design and interpretation of the experiments reported in Tables 1 and 2. The resulting expressions are:

$$F = (GK)^{n-1} \sum_{i=1}^{n} (RK)^i \Big/ \left[ \sum_{i=0}^{n-1} (GK)^i + (GK)^{n-1} \sum_{i=1}^{n} (RK)^i \right] \tag{1'}$$

$$\phi = \sum_{i=0}^{n-1} (GK)^i \Big/ \left[ \sum_{i=0}^{n-1} (GK)^i + (GK)^{n-1} \sum_{i=1}^{n} (RK)^i \right] \tag{2'}$$

where $G$ is the volume ratio of upper to lower phase in each of the contactors 1 to $(n - 1)$ inclusive and $R$ is the corresponding ratio in each of the contactors $n$ to $(2n + 1)$ inclusive.

From Table 1, it may be seen that Th may be separated readily from Sc and from Zr. The effectiveness of sacrificing yield in return for purity is also demonstrated by the data of this table.

*Mutual Separation of Sc, Th, and Zr by use of TBP-$HNO_3$ Systems.* In Table 2, the results of operating three different TBP-$HNO_3$ systems are presented as three different runs. In Runs 1 and 3, Th and Zr are respectively isolated as the single product

component in the upper phase. In Run 2, Sc is isolated as the single product component in the lower phase.

## DISCUSSION

From the data of Fig. 1, the $K$ values of Sc and Th at 7 M HCl are taken as 14·0 and 0·085, respectively, the $\beta$ value being 165. Considering the reciprocity relations leading to equation (3) and assuming an $R$ to $G$ ratio of 0·750, it may be seen that to a first approximation, equal degree of mutual separation of Sc and Th may be obtained operating with $R = 0{\cdot}793$ and $G = 1{\cdot}057$. Using the conveniently measured volumes of feed, scrub and solvent of 25 ml, 75 ml, and 80 ml, respectively, respective values of $R$ and $G$ are 0·800 and 1·07. The results of Run No. 2, Table 1, are seen to compare very favourably with the theoretical values obtained by use of equations (1′) and (2′).

The data of Run No. 3, Table 1, illustrate the enhanced purity of Sc product (with respect to Th contamination) obtained in return for a slight sacrifice in yield. (The $DF$ for Run No. 3 exceeds that for Run No. 2 by a factor greater than 100; see equation 9). It is to be noted that the lower yield of Sc is obtained by decreasing $R$ and $G$ rather than by decreasing the molarity of HCl or the molarity of TBP, since either of these latter changes would have affected $\beta$ adversely.

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The data of Run No. 4, Table 1, illustrate the enhanced purity of Th product obtained in return for a slight sacrifice in yield. (The DF for Run No. 4 exceeds that for Run No. 2 by a factor greater than 100; see equation 9. Compare, also, Run No. 1 of Table 1.) By reference to Fig. 1, it is seen that the results of Run No. 4 should be duplicated by operating at 8 M HCl with $R$ and $G$ reduced by a factor of 0·21. This has been found to be true.

The data of Run No. 1, Table 2, show the separation of a Th product, the decontamination with respect to Sc and Zr being quite satisfactory. It is to be noted from Fig. 3 that the $\beta$ for Th with respect to Sc has the same value at 2 M and at 8 M $HNO_3$ and higher values at intermediate acidities. However, since the point at which the Zr curve crosses the Sc curve had not been established, 2 M $HNO_3$ was chosen for this separation.

From Fig. 3, it may be seen that operation at 6 M $HNO_3$ would be favourable to separation of Sc product. However, all $K$'s are awkwardly large. In this case, in place of using very small $R$ and $G$ values it is preferable to use a diluted solvent, since with dilution the $K$ values for Sc and Th are lowered at approximately equal rates (see Figs. 4 and 5) but much more rapidly than is the $K$ value for Zr. Consequently, dilution of the TBP favours the separation of Sc from Zr (compare Figs. 3 and 6.) The data of Run No. 2, Table 2, show the results of this mode of operation, designed so that Th and Sc should be separated from each other to equal extent. The Sc product is seen to be of high purity.

The data of Run No. 3, Table 2, illustrate the separation of a Zr product. The instability of the diluent toward higher concentrations of $HNO_3$ dictated the choice of 12 M $HNO_3$. (More concentrated solutions of $HNO_3$ may be used in small-scale experiments of short duration.) A comparison of Figs. 3 and 6 shows the advisability of using a diluted TBP.

In the 12 M $HNO_3$-TBP system the operational TBP dependencies for Zr and Th are respectively slightly less than third power and slightly more than fourth power. Consequently, although the $\beta$ for Zr with respect to Th is only three in the 12 M $HNO_3$-

undiluted TBP system (Fig. 3), the $\beta$ in the 12M $HNO_3$-25%[11] system (Fig. 6) is 16 and that in the 12M $HNO_3$-20% TBP[11] system is 40, the respective $K$ values for Zr and Th in this last system being 16 and 0·40. The data of Table 2, Run No. 3, show that the isolation of a Zr product of high purity is readily accomplished.

It is apparent that by use of countercurrent distribution[12] both the TBP-HCl and TBP-$HNO_3$ systems may be used in the analytical applications of these separations procedures; and they have been so used in this laboratory for the separation of each of the three elements discussed.

It is equally apparent that the systems may be used in large-scale operations by use of discontinuous countercurrent extraction[10] and by use of continuous countercurrent extraction in those instances in which phase disengagement is sufficiently rapid.

[12] L. C. CRAIG *Analyt. Chem.* **21**, 85 (1949) describes a sequence, designated by him as countercurrent distribution, in which each portion of upper (or lower) phase remains in a given contacter and the separate portions of opposing phase are cycled through the assembly in series.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 229 to 232. Pergamon Press Ltd., London

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# A MANGANESE-DIOXIDE PROCEDURE FOR ISOLATION AND CONCENTRATION OF PROTACTINIUM FROM IRRADIATED THORIUM COMPOUNDS*

LEONARD I. KATZIN† and RAYMOND W. STOUGHTON‡

(*Received* 13 *June* 1956)

**Abstract**—Traces of protactinium may be coprecipitated on manganese dioxide with good recovery from solutions 1N to 4N in nitric acid upon precipitating 1·5 g of dioxide per litre by the addition of potassium permanganate to manganous nitrate in excess. Good separation is obtained from macro concentrations of thorium nitrate. In concentrations up to 0·65M the thorium does not interfere with the precipitation, while at twice this concentration definite interference is found owing to the effect on the physical properties of the solution. With the aid of hydroxylamine to redissolve the dioxide, it is possible to concentrate the protactinium with respect to carrier by a factor of 100 per cycle. Hydrogen peroxide, sodium nitrite, and formic acid were less satisfactory reagents. Simultaneous purification from thorium and uranium may be achieved.

Thorium is found to carry well in trace concentrations, but the efficiency of this process falls off with increasing thorium concentration.

## 1. INTRODUCTION

THORIUM is used as the target material in neutron or deuteron irradiations designed to yield the synthetic isotopes of uranium, $U^{232}$ and $U^{233}$. The initial reaction product may be either a thorium isotope or a protactinium isotope, but in neither case is the uranium nucleus formed directly. In most cases the concentration of product isotopes is a minute fraction of a part per million of the original thorium. Since this thorium may contain in the neighbourhood of one to several parts per million of natural uranium impurity, it is impractical to obtain pure synthetic uranium isotopes by allowing decay of the intermediate protactinium and then separating out uranium. It is accordingly necessary to investigate the isolation of the intermediate protactinium and its freeing from natural uranium as well as from thorium.

A method which has already been applied to the separation of protactinium from irradiated thorium salts is based on the coprecipitation of protactinium with manganese dioxide.[1] It is the purpose of this paper to give the results of studies on the conditions for this separation, the efficiency of separation from thorium and uranium, and the possibilities of a concentration process which does not involve the use of alternate carriers such as zirconium phosphate.

* Based on work performed under the Manhattan Project ("Metallurgical Laboratory") in the interval April to September 1943 and recorded in Reports CC-739, CC-887, and ANL-4035.

† Argonne National Laboratory, Lemont, Illinois.

‡ Oak Ridge National Laboratory, Oak Ridge, Tenn.

[1] G. T. SEABORG, J. W. GOFMAN, and R. W. STOUGHTON *Production and Separation of* $U^{233}$. National Nuclear Energy Series, Plutonium Project Record, Vol. 17B, Div. IV, pp. 31–45. McGraw-Hill Book Company, Inc., New York, (1952)

## 2. EXPERIMENTAL WORK

The system chosen was a solution of thorium nitrate containing nitric acid and manganous nitrate in excess. The desired amount of manganese dioxide (usually 1·5 g per litre) was precipitated by the addition of the proper amount of potassium permanganate. A digestion with warming was usually allowed. Later experiments have shown such heating to be essential for good carrying.[2] Experiments were customarily performed with solutions of 0·1 ml total volume, the precipitate being separated by centrifugation. Reagents were added, and supernatants were removed with the aid of glass capillaries. For determination of the behaviour of the tracers used ($Pa^{233}$ and $UX_1$), material was mounted on platinum disks and measured with the Geiger-Müller counter (having a thin-mica end window) standard in the laboratory.

The completeness of the manganese dioxide precipitation and the physical characteristics of the precipitate were shown to be dependent on the nitric-acid concentration. The range from less than 1 N to 4 N or 5 N was shown to be safe by experiments in which macro quantities of the dioxide were precipitated and the manganese in the precipitate was determined. The concentration of thorium nitrate also affected the precipitation strongly in the higher ranges of thorium concentration, in large part by affecting the physical properties of the solution. The range up to 360 g of thorium nitrate tetrahydrate per litre (0·65 M) was found to give good precipitation of the manganese dioxide, while at twice this concentration it was poor.

With the aid of $UX_1$ tracer, the carrying of thorium on the manganese dioxide was also determined. As the results show (Table 1), the carrying is a function of thorium concentration, with trace concentrations of thorium being carried essentially

TABLE 1.—CARRYING OF $UX_1$ TRACER BY 1·5 G OF $MnO_2$ PER LITRE FROM THORIUM NITRATE SOLUTIONS

| Conc. thorium nitrate tetrahydrate, g/litre | Per cent $UX_1$ carried |
|---|---|
| 0·1 | 99 |
| 10 | 20 |
| 120 | 5 |
| 360 | 0·3 |

completely. Detectable amounts of thorium are carried by manganese dioxide from concentrations of thorium nitrate in the normal range (0·02 M to 0·65 M). This can be demonstrated by dissolving the washed precipitate in hydrogen peroxide, which gives a residue of insoluble thorium-peroxide compound. In addition to the thorium itself, members of its decay chain are carried fairly well. This produces a background of radioactivity in tracer experiments which must be taken into consideration. The principal activities carried seem to be ThB and ThC, the latter in an amount two or three times that which would normally be in radioactive equilibrium with the former. Others have since found that the carrying of $UX_1$ tracer is decreased, without affecting protactinium carrying,[3] by increasing nitric acid concentration.

[2] J. P. HUNT, J. HALPERIN, and R. W. STOUGHTON Private communication.
[3] J. HALPERIN Private communication, 1946.

Protactinium tracer was found to be carried well by manganese dioxide in the range of optimal precipitation. Yields of over 95 per cent could be demonstrated by slurrying the precipitate onto platinum counting disks for measurement. Lower recoveries (75 to 90 per cent) were found when the precipitate was dissolved in the centrifuge cone and the resulting solution was evaporated onto the counting disk. Some of the lost tracer could be recovered from the glassware used on washing with hydrofluoric acid, indicating that the loss occurs in the process of dissolving the manganese dioxide. This fact and the irregular adsorption of protactinium on glass rendered experimental results somewhat erratic.

Following a first precipitation of manganese dioxide from thorium solutions, the $Pa^{233}$ carried is still quite dilute. It was thought that cycles consisting of manganese dioxide precipitation, dissolution of the precipitate in a small volume of reagent, and reprecipitation of a small fraction of the manganese by addition of permanganate could be used to achieve concentration and further purification simultaneously. Within the scale of operations available in the laboratory this proved feasible, and on the basis of these results a similar process was later applied to larger scale operations at the Clinton Laboratories.[4]

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Since hydrochloric acid is undesirable for use in metal equipment, especially when chlorine will be formed from it, other agents were investigated for dissolving the manganese dioxide. The foaming of hydrogen peroxide was not a desirable characteristic for work with radioactive solutions, and the instability of the reagent was considered another drawback. Hydrogen peroxide also tended to form insoluble thorium peroxide with the coprecipitated thorium. Sodium nitrite reacted with freshly precipitated dioxide but was not satisfactory for work with commercial material. Formic acid was investigated and was shown to dissolve the dioxide well when heated. The number of factors entering into its use (rate of reaction, stability, gas evolution, etc.) made it only partially satisfactory. Hydroxylamine proved to be a good choice, however, reacting stoichiometrically even in the cold. Although the hydrochloride was used in the tests, it was not felt that the amount of chloride introduced would be of significance even in metal equipment.

Using hydroxylamine, it has been possible to obtain a concentration factor as high as 100 per cycle. Since such a factor rapidly alters the scale of operations, a considerably smaller one can be used satisfactorily. Experiments in which the manganese was reprecipitated without change of volume showed that four such precipitations could give as much as 80 to 85 per cent recovery. Experiments were also performed in which starting volumes of about 10 ml were reduced to 0·1 ml by the first cycle, with the second precipitation giving the activity on 0·15 mg or less of manganese dioxide. Yields of 85 per cent have been obtained through the two cycles of such experiments. In addition to low-activity tracer experiments of this type, the procedure was tested on thorium oxycarbonate that had been exposed for a long time to slow neutrons produced in the St. Louis cyclotron. Starting with a volume of 10 to 15 ml of thorium nitrate solution, the $Pa^{233}$ activity came satisfactorily with the manganese dioxide and was concentrated in the second precipitate as scheduled. Approximately 0·05 $\mu$g was concentrated readily in this fashion. Using $Pa^{231}$, carrying was still excellent at a Pa : $MnO_2$ weight ratio 1 : 20,000, and 88 % at 1 : 200.

[4] R. W. Stoughton, F. H. Steahly, P. A. Schulze, and M. E. Bishop Report CC-1024, Nov. 8, 1943.

The eventual recovery of $U^{233}$ following this procedure could be achieved through storing the last manganese dioxide precipitate to allow the desired protactinium decay, dissolving the manganese dioxide, and reprecipitating it. The precipitate would separate off most of the remaining protactinium radioactivity, allowing convenient recovery of the uranium from the supernatant by solvent extraction. The solvent extraction could be carried out without the precipitation of the protactinium, but it is rendered easier by prior removal of the radiation source, which might necessitate shielded operation. Experiments with $U^{232}$ tracer showed that the carrying of uranium by manganese dioxide was low enough ($<1\%$) to give the required purification of the protactinium from the natural uranium impurity of the thorium irradiated originally.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 233 to 242. Pergamon Press Ltd., London

# RAPID ION-EXCHANGE TECHNIQUES FOR RADIOCHEMICAL SEPARATIONS

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(*Received* 14 *May* 1956)

**Abstract**—The short-lived nuclear isomers, $Pb^{207m}$ (0·8 sec) and $Ir^{191m}$ (4·9 sec) have been identified and characterized after rapid anion-exchange separation from their long-lived parents, $Bi^{207}$ (8 years) and $Os^{191}$ (16 days). Diffusion of daughter activities from the resin to solution phase is sufficiently rapid to permit satisfactory separation from the parent activities.

In the strong base anion exchanger used, the diffusion coefficient of tracer Pb(II) was found to be $7{\cdot}8 \times 10^{-6}$ cm²/sec at 25°C. The yield of the $Pb^{207m}$ separation, as calculated from diffusion theory and the measured diffusion coefficient of Pb(II), is in fair agreement with that observed. Results are discussed in regard to general applicability of the ion-exchange technique for rapid separations.

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FOR establishing genetic relationships in nuclear decay schemes, the techniques of chemical separation have for many years been an important tool of nuclear chemistry. While the method of delayed coincidences is successful in establishing half-lives in the microsecond range, it becomes more difficult to apply as the half-life of the daughter becomes longer than, say, $10^{-3}$ sec, due to the large random background. The object of the present inquiry was to investigate the applicability of ion exchange for separating daughter activities having half-lives in the range of a few milliseconds to a few seconds.

In the past only a few techniques have been exploited which enable separations to be made in less than a second or two; those which have been described usually involve diffusion of gases from solids or liquids as the primary rate-controlling factor. Typical examples are the classical emanation techniques originated by HAHN[1] and the gas-sweeping methods[2] for separating short-lived rare-gas activities from solids or solutions. These types of separations, however, are limited in their general applicability.

Since conditions are presently available in the literature for separating a large number of elements by ion exchange, use of recently developed anion- and cation-exchange materials should offer a more general means for effecting rapid separations.

In the present work, an anion-exchange resin has been used for separations of two short-period activities, $Pb^{207m}$ (0·8 sec) and $Ir^{191m}$ (4·9 sec) from their long-lived parents, $Bi^{207}$ and $Os^{191}$, respectively. A strong-base quaternary amine polystyrene-divinyl benzene resin was used. Certain elements are adsorbed very strongly from

[1] See, e.g., A. C. WAHL and N. A. BONNER Editors *Radioactivity Applied to Chemistry* p. 284, John Wiley and Sons, Inc., New York (1951).

[2] (a) E. L. BRADY and N. SUGARMAN *National Nuclear Energy Series* IV, 9, *Part* V, p. 613, McGraw-Hill Book Co., Inc., New York (1951); (b) C. R. DILLARD, R. M. ADAMS, H. FINSTON, and A. TURKEVICH, *loc. cit.*, p. 616.

hydrochloric-acid solution by this resin,[3] and use has been made of this behaviour for many separations.

For the parent-daughter elements mentioned, the distribution coefficients, defined as $D_v$ = amount adsorbed per litre resin bed/amount per litre solution, are $3 \times 10^4$ for Bi(III), 9 for Pb(II) in 0·5 M HCl[3, 4], and $10^3$ for Os(IV), ~1 for Ir(III) in 6 M HCl[3]. On the basis of these large differences in distribution coefficients, excellent column separation of these pairs of elements may be achieved by conventional column-elution techniques.

Separations of daughter activities with very short half-lives, however, depend on whether the daughter activity may be eluted rapidly enough from the resin under conditions where the parent activity, for the most part, remains adsorbed. If the mean time for diffusion of the daughter out of the resin is not too long compared to the mean life of the daughter, separation should be possible. Apparently these conditions are met by the isomers studied. When resin containing adsorbed $Bi^{207}$ (Bi(III)) or $Os^{191}$ (Os(IV)) was rapidly eluted with appropriate hydrochloric-acid solution, an appreciable fraction of daughter activity which quickly decayed was observed in the effluent stream. These experiments confirmed the existence of short-lived isomers in the decay schemes of $Bi^{207}$ and $Os^{191}$.

## 1. NUCLEAR DATA

The pertinent nuclear information for the decay of $Pb^{207}$ and $Ir^{191}$ to metastable states in $Pb^{207}$ and $Ir^{191}$ is shown in Fig. 1. The results of the present experiments on the half-lives of the metastable states are shown encircled. In each case the nuclear information previously available made the existence of a metastable level very likely.

MCGOWAN[5] reported that no prompt ($\beta$, $\gamma$) coincidences were observed in the decay of $Os^{191}$. After the present experiment had been completed, but prior to publication in the open literature, the isomer was independently found by NAUMANN and GEBHART,[6] who flamed platinum plates containing $Os^{191}$ to volatilize Os as the tetroxide away from $Ir^{191m}$, and by FISCHER,[7] who produced the isomer by bombarding Ir with 31·5 MeV protons.

A suggestion that $Bi^{207}$ decayed via an isomeric state in $Pb^{207}$ previously found[8] in pile-neutron-irradiated $Pb^{207}$ was made by GRACE and PRESCOTT[9] and by CAMPBELL.[10] On theoretical grounds, GOLDHABER and SUNYAR[11] and PRYCE[12] assigned the activity to a metastable state of $Pb^{207}$ and characterized the decay with the spin assignment $i13/2(M4)\ f5/2(E2)p\ 1/2$. The implication that the state could be produced by an $(n, n')$ reaction was later verified by STELSON and CAMPBELL,[13] who

[3] The adsorbability behaviour of many elements in hydrochloric acid has been recently summarized for this resin. K. A. KRAUS and F. NELSON, Anion Exchange Studies of the Fission Products, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy* P/837, *Volume* 7, p. 113, Session 9B.1, United Nations (1956).
[4] F. NELSON and K. A. KRAUS *J. Amer. Chem. Soc.* **76**, 5916 (1954).
[5] F. K. MCGOWAN *Phys. Rev.* **93**, 163 (1954).
[6] R. A. NAUMANN and J. B. GEBHART *Phys. Rev.* **96**, 1452 (1954).
[7] V. K. FISCHER *Phys. Rev.* **99**, 764 (1955).
[8] E. C. CAMPBELL and M. GOODRICH *Phys. Rev.* **78**, 640 (1950).
[9] M. A. GRACE and J. R. PRESCOTT *Phys. Rev.* **84**, 1059 (1951).
[10] E. C. CAMPBELL, Oak Ridge National Laboratory Report ORNL-1164 (1951) (unpublished).
[11] M. GOLDHABER and A. W. SUNYAR *Phys. Rev.* **83**, 906 (1951).
[12] M. H. L. PRYCE *Proc. Phys. Soc.* (London), **A65**, 773 (1952).
[13] P. H. STELSON and E. C. CAMPBELL *Phys. Rev.* **97**, 1222 (1955).

studied the cross-section for the reaction $Pb^{207}$ $(n, n')$ $Pb^{207m}$, as a function of neutron energy.

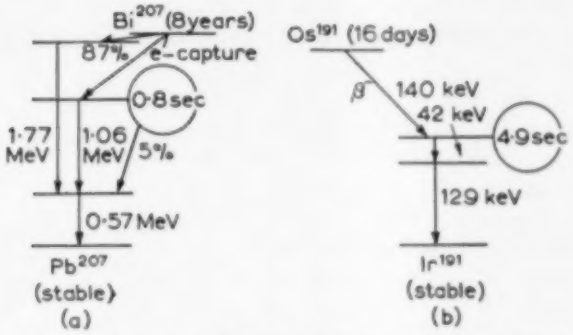


FIG. 1.—Decay schemes of $Bi^{207}$ and $Os^{191}$. The data contributed in the present experiment are shown encircled.

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## 2. EXPERIMENTAL AND RESULTS

(a) *$Pb^{207m}$*. $Bi^{207}$ was prepared by proton bombardment of Pb in the ORNL cyclotron.[14] The lead target was dissolved in nitric acid and $Bi^{207}$ separated and purified by anion-exchange methods described earlier[4]. A small aliquot of purified $Bi^{207}$ (about $10^5$–$10^6$ d/min) was diluted to 10 c.c. with 0·5 M HCl and about 50 mg of chloride-form strong-base anion-exchange resin (Dowex-1, 230–370 mesh, 10% divinyl benzene) was added. After shaking resin and solution for a few minutes, the $Bi^{207}$ as a chloride complex was essentially completely adsorbed by the resin. The resin was placed on a sintered glass filter and about 1 ml of liquid (0·5 M HCl) was forced through the resin into a test-tube by means of a hypodermic syringe. Following immediate transfer of the test-tube into a well-type NaI(Tl) scintillation counter, a high counting-rate was observed which decayed rapidly with the expected half-life of 0·8 sec. In later work it was found convenient to introduce the resin above a glass-wool filter directly into the hypodermic syringe. Such an apparatus, which is easily portable, has been used by the authors in connection with lecture demonstrations.

The half-life of $Pb^{207m}$ was also obtained by measuring the effluent counting-rate as a function of distance downstream from the resin for constant flow of known velocity. A schematic diagram of the apparatus for continuous recirculation of effluent is shown in Fig. 2. As the position $x$ of the detector below the uniform-bore tube is varied, the counting-rate is expected to decrease according to $e^{-(\lambda x/v_0)}$, where $v_0$ is the flow velocity and $\lambda$ is the decay constant. The horizontal tube can be moved through the counter shield. To avoid complications associated with the nonuniform velocity profile of laminar flow and also to provide a direct means of measuring the flow velocity, air was allowed to leak into the system to form uniform bubbles spaced at regular intervals. The time taken for bubbles to travel the distance between two markers 100 cm apart on the tube was measured with a stop-watch during each of the counting intervals. The mean of seventy-two readings was 4·54 sec, with a standard deviation of 0·09 sec, giving $v_0 = 22$ cm/sec.

[14] We are indebted to Mr. JOHN MARTIN of the Cyclotron Group of ORNL for the preparation of this activity.

Results of the experiment to determine the half-life of $Pb^{207}$ are shown in Fig. 3. Between 50,000 and 100,000 counts were taken for each point. A background of 17·6 counts/sec, measured on stopping the flow, was subtracted from the observed counting-rates to give the points plotted. The straight line that gives the best fit corresponds to

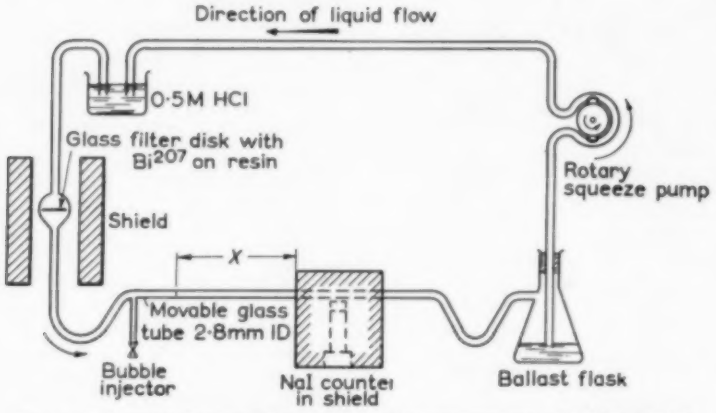


FIG. 2.—Schematic diagram of an apparatus for measurement of $Pb^{207m}$ half-life.

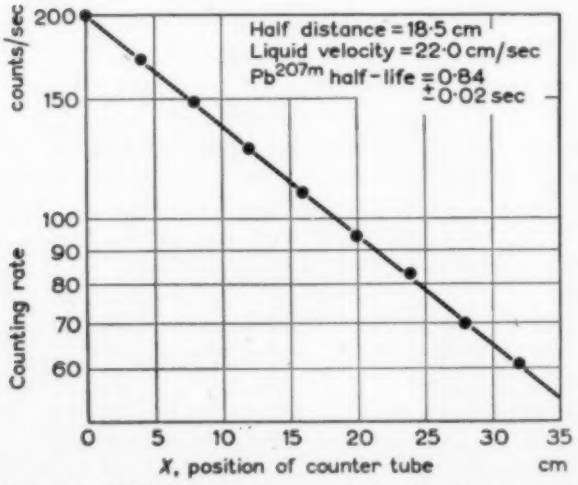


FIG. 3.—Attenuation of $Pb^{207m}$ activity downstream from source in continuous-flow experiment.

a half-distance, $x_{1/2}$, of 18·5 cm and gives a half-life of 0·84 sec for $Pb^{207m}$, with a probable error of 2%.

$Pb^{207m}$ in the effluent stream was also examined with a NaI(Tl) scintillation spectrometer. The gamma energies observed were in good agreement with those in

the decay scheme (Fig. 1a) and with the values 0·57 ± 0·02 and 1·06 ± 0·02 MeV. measured for radiations from the short-lived activity of reactor-neutron-irradiated lead[10, 15] produced by the reaction $Pb^{207}(n, n')Pb^{207m}$. The measured half-life, 0·84 ± 0·03 sec[15] of the directly produced isomer is in good agreement with that obtained for the separated isomer.

(b) *$Ir^{191m}$*. $Os^{191}$ was prepared by neutron irradiation of 0·1 g of osmium tetroxide in the Low Intensity Training Reactor (LITR) at ORNL. The irradiated sample was dissolved in 6 M HCl containing 1 ml of ethyl alcohol, and the resulting solution refluxed for about 5 hours near 100°C to convert the osmium to the red hexachloro complex of Os(IV), $OsCl_6^{-2}$.[16] An aliquot containing about 0·01 millicurie $Os^{191}$ was

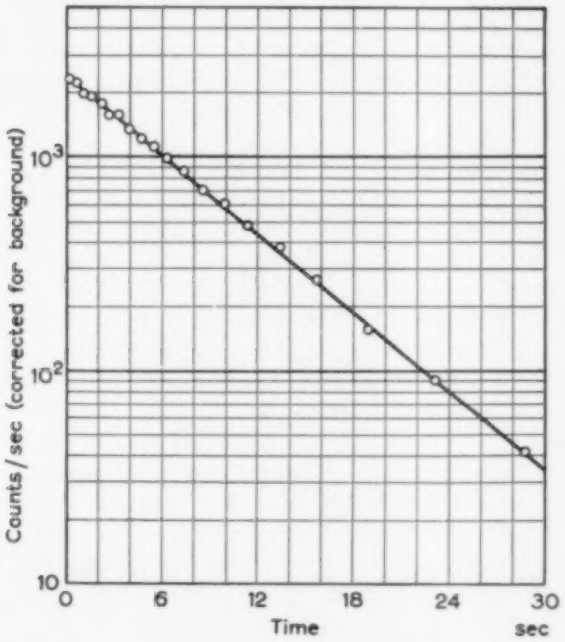


FIG. 4.—Decay rate of separated $Ir^{191m}$.

added to a small (1 ml) column of resin which had been pretreated with 6 M HCl. The osmium complex adsorbed as a reddish-brown band at the top of the resin bed. When 6 M HCl was rapidly forced through the bed with a hypodermic syringe, a short-lived activity attributable to $Ir^{191m}$ was found in the effluent, indicating that decay of $Os^{191}$ ($OsCl_6^{-2}$) adsorbed by the resin gives rise to appreciable amounts of weakly adsorbed $Ir^{191m}$ species. The fact that Ir(IV) as $IrCl_6^{-2}$ adsorbs very similarly to $OsCl_6^{-2}$, $D_v \cong 10^3$ at the HCl concentration used for elution,[3] while Ir(III) as $IrCl_6^{-3}$ is weakly adsorbed, suggests that an appreciable fraction of the $Ir^{191m}$ daughter species appears as $IrCl_6^{-3}$ on decay of $Os^{191}$ ($OsCl_6^{-2}$).

The rate of decay of separated $Ir^{191m}$ is shown in Fig. 4. The counting-rate at each

[15] E. C. CAMPBELL, Oak Ridge National Laboratory Reports ORNL-1365 (1952) and ORNL-1798 (1954).
[16] R. GILCHRIST *Chem. Rev.* **32**, 277 (1943).

point is corrected for a background of 296 counts/sec. The sample had an initial counting rate of about $2{\cdot}4 \times 10^3$ counts/sec and the counting rate followed a straight line on a semilog plot. The average half-life of two measurements was $4{\cdot}9 \pm 0{\cdot}1$ sec. This value is in good agreement with the value ($4{\cdot}91 \pm 0{\cdot}14$ sec) reported by FISCHER[7].

Separated $Ir^{191m}$ was also examined with a multichannel analyser, and the energy of the gamma ray observed was consistent with that given in Fig. 1(b).

## 3. APPLICABILITY OF ION EXCHANGE TO RAPID SEPARATIONS

(a) *Theoretical considerations.* Since the foregoing experiments demonstrated that ion-exchange resins could be used satisfactorily for rapid separations of short-lived daughter activities with half-lives of the order of a second, calculations based on diffusion-theory and decay-rate considerations were made to estimate the range of applicability of the technique. For these calculations the relative adsorbabilities of the parent and daughter, their rates of radioactive decay, and their rates of diffusion in the resin need to be considered.

If a parent-daughter system is chosen in which the parent is strongly adsorbed and the daughter is weakly adsorbed, the concentration of the parent in a recirculating system should remain essentially constant and high in the resin compared to its concentration in solution. Thus, the resin phase can be looked upon as a daughter production source, producing short-lived daughter species at a constant rate governed by the decay constant of the parent. If the daughter in the short-lived metastable state (called $Z^*$) can diffuse out of the resin spheres sufficiently rapidly into the fast-flowing liquid medium, separation should be observed on counting either the liquid downstream or by counting the resin itself.

The yield of the separation process $Y$ is defined as that fraction of $Z^*$ atoms produced which decay outside the resin. A theoretical expression for $Y$ can be derived from diffusion theory for a single resin bead in terms of parameters which describe the system. It is assumed that daughter species are produced uniformly throughout a resin sphere of radius $R$ at a constant rate $Q$ per unit volume, and that the boundary condition on the concentration of the diffusing species $\varphi(r)$ is $\varphi(R) = 0$. The diffusion equation may be written

$$-\mathscr{D}\nabla^2\varphi(r) + \lambda\varphi = Q, \tag{1}$$

($r \leq R$) where $\mathscr{D}$ is the diffusion coefficient of $Z^*$ species inside the resin sphere and $\lambda$ is its radioactive decay constant. Equation (1) represents the equality for each volume element of the sphere between the number of $Z^*$ atoms which are produced per second with the number of $Z^*$ atoms which either diffuse out (first term) or decay (second term) per second. A solution of (1) satisfying the boundary condition is

$$\varphi(r) = \frac{Q}{\lambda}\left[1 - \frac{R \sinh \sqrt{\frac{\lambda}{\mathscr{D}}}\, r}{r \sinh \sqrt{\frac{\lambda}{\mathscr{D}}}\, R}\right] \tag{2}$$

The yield $Y$, as previously defined, is given by

$$Y(u) = \frac{4\pi R^2 \left[-\mathscr{D}\frac{d\varphi}{dr}\right]_{r=R}}{\frac{4}{3}\pi R^3 Q} = \frac{3}{u^2}[u \coth u - 1] \tag{3}$$

where $u = \sqrt{\frac{\lambda}{\mathscr{D}}}\,R$. The function $Y(u)$ is plotted in Fig. 5. For $u \gg 1$ (low yield) $Y(u) = 3/u$.

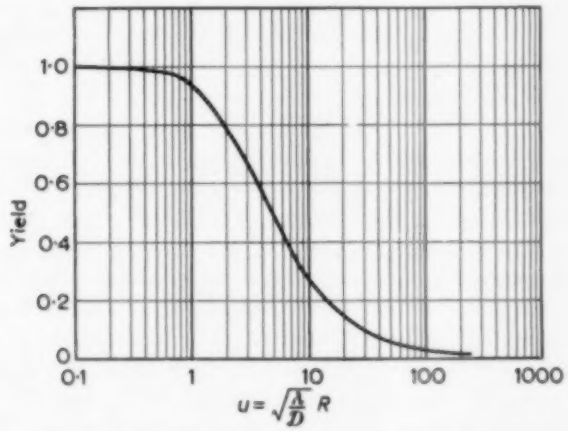


FIG. 5.—Yield for ion-exchange separation as a function of parameter $u = \sqrt{\lambda/\mathscr{D}}\,R$.

Little information is available regarding diffusion coefficients $\mathscr{D}$ in anion-exchange resins, particularly for complex ions. However, self-diffusion coefficients measured for a few simple anions, i.e. $Cl^-$, $Br^-$, etc,. and oxygenated ions, $BrO_3^-$, $PO_4^{-3}$, etc., have been found[17] to range from about $10^{-7}$ to $10^{-8}$ cm²/sec in a polystyrene-divinyl benzene strong-base resin containing 6% divinyl benzene. On the other hand, the self-diffusion coefficient of a cation ($Na^+$) was found to be of the order of $10^{-5}$ cm²/sec in the same anion-exchange resin. These values of diffusion coefficients along with the equations above permit an estimation of the yields that might be expected for separations of short-lived daughter elements.

The yields for the separation of daughter activities with half-lives ranging from $10^{-4}$ to one sec were calculated from theory for values of $\mathscr{D}$ ranging from $10^{-5}$ to $10^{-8}$ cm²/sec, assuming a resin-bead radius, $R = 10^{-3}$ cm. Calculations were based on the relation, $u = \sqrt{\frac{\lambda}{\mathscr{D}}}\,R$, and Fig. 5 or (for low yields) the approximation, $Y = 3/u$. The results are tabulated in Table 1. Since yields as low as 0·02 (two per cent) should be experimentally measurable at rapid flow-rates, it should be possible, according to the results in Table 1, to detect separation of daughter activities with half-lives of the order of a millisecond from small resin beads when diffusion coefficients of the daughter species are favourable.

TABLE 1.—SEPARATION OF A SHORT-LIVED DAUGHTER ACTIVITY FROM A LONG-LIVED PARENT (RADIUS, $R = 10^{-3}$ CM)

| Half-life (sec) | Theoretical yield | | | |
|---|---|---|---|---|
| | $\mathscr{D} = 10^{-8}$ | $10^{-7}$ | $10^{-6}$ | $10^{-5}$ cm²/sec |
| $10^{-4}$ | 0.004 | 0·01 | 0·04 | 0·10 |
| $10^{-3}$ | 0·01 | 0·04 | 0·10 | 0·32 |
| $10^{-2}$ | 0·04 | 0·10 | 0·32 | 0·70 |
| $10^{-1}$ | 0·10 | 0·32 | 0·70 | 0·96 |
| 1 | 0·32 | 0·70 | 0·96 | 0·99 |

(b) *Comparison of the theoretical and observed yields for $Pb^{207m}$ separation.* The theoretical yield was calculated for one of the systems studied, $Bi^{207}$—$Pb^{207m}$, after experimentally measuring the diffusion coefficient of Pb(II) in the resin phase. Since Pb(II) is the more stable oxidation state of lead, it will be assumed that Pb(II) forms on decay of the bismuth parent. A shallow-bed elution technique similar to that of BOYD, ADAMSON, and MYERS[18] was used to determine the self-diffusion rate of a long-lived Pb(II) tracer ($Pb^{210}$, Ra$D$ $t_{1/2} = 22$ years) in the resin. After removing the $Bi^{210}$ daughter by anion exchange[3], the $Pb^{210}$ tracer in 0·5 M HCl was equilibrated several hours with 230–270 mesh anion-exchange resin. The average "wet" radius, determined from photomicrographs of the beads in 0·5 M HCl, was $3{\cdot}5 \times 10^{-3}$ cm. A portion of the $Pb^{210}$-equilibrated resin was transferred to a small column, 0·12 cm² in area, to form a shallow bed about a millimetre in depth. The counting-rate of the bed was measured as a function of time while rapidly eluting with 0·5 M HCl. Results of a typical experiment carried out at a solution flow-rate of 4·4 cm/sec are shown in Fig. 6. The plot of log counting-rate of the resin, corrected for a small $Bi^{210}$ and room background, vs. time is approximately linear. The average half-time for removal in three separate experiments was $11{\cdot}0 \pm 0{\cdot}3$ sec and was independent of flow-rate in the region investigated, 0·5 to 6 cm/sec.

According to diffusion theory, the concentration of the diffusing species in the resin decreases as $e^{-\lambda_r t}$ where $\lambda_r = \dfrac{\mathscr{D}\pi^2}{R^2}$ after an initial transient effect associated with the decay of higher diffusion modes has died out. The average value of $\lambda_r$ from the three experiments was 0·063 sec$^{-1}$, corresponding to a diffusion coefficient, $\mathscr{D}$, of Pb(II) in the resin of $7{\cdot}8 \times 10^{-8}$ cm²/sec at $25{\cdot}0 \pm 0{\cdot}3$°C. From $u = \sqrt{\dfrac{\lambda}{\mathscr{D}}}\, R$, the decay constant for $Pb^{207m}$, $\lambda = 0{\cdot}845$ sec$^{-1}$, and $R = 3{\cdot}5 \times 10^{-3}$ cm, a value $u = 12{\cdot}1$ is calculated. The theoretical yield corresponding to $u = 12{\cdot}1$ (Fig. 5) is 0·227, in good agreement with the experimental yield of 0·194 discussed below.

The experimental yield for the separation of $Pb^{207m}$ from $Bi^{207}$ was determined by recycling a solution of $Bi^{207}$ in 0·5 M HCl, through a shallow resin bed containing the

[19] G. E. BOYD, A. W. ADAMSON and L. S. MYERS *J. Amer. Chem. Soc.* **69**, 2863 (1947).

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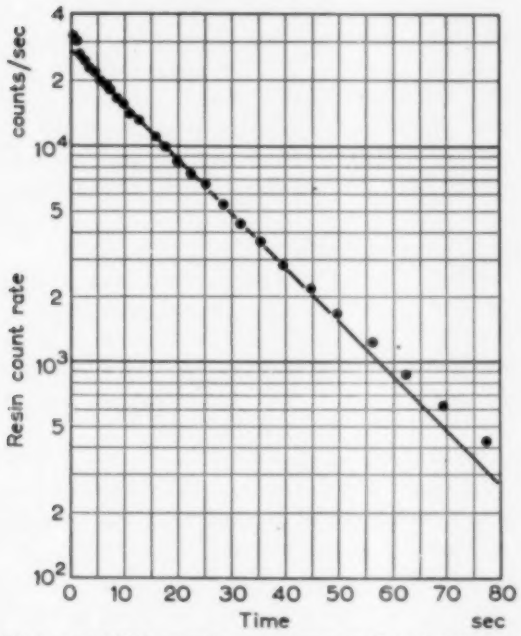


FIG. 6.—Elution of $Pb^{210}$ from anion-exchange resin (0·5 M HCl, flow-rate 4·4 cm/sec).

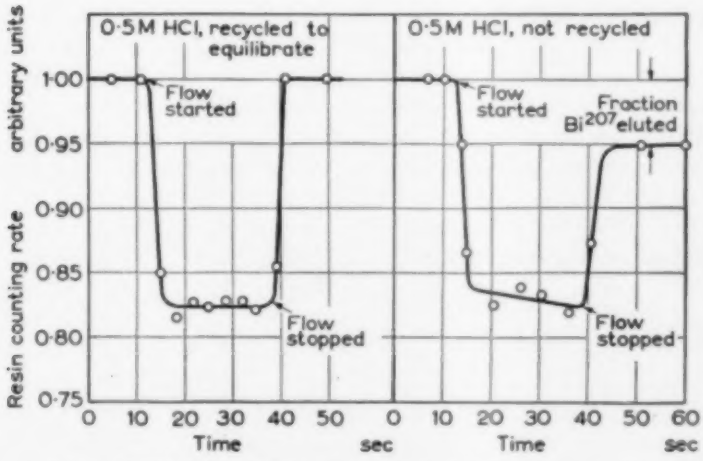


FIG. 7.—Rapid elution of resin containing adsorbed $Bi^{207}$ (flow-rate 17 cm/sec).

equilibrium concentration of $Bi^{207}$. Since the distribution coefficient for Bi(III) is large, the counting-rate of the solution (per unit volume) is negligible compared to the counting-rate of the resin bed. Hence the decrease in the counting-rate of the small resin bed under conditions of rapid flow gives the yield for the separation. Typical results are shown in Fig. 7(a). The counting-rate of the resin decreases about 18% during the period of rapid flow (17 cm/sec) and then increases to the original counting-rate when the flow is stopped. The observed decrease is associated with the removal of $Pb^{207m}$ from the resin into the flowing liquid during the short interval between production and decay.

From the decay scheme it can be estimated that approximately 93% of the gamma counting-rate of $Bi^{207}$ in a NaI crystal (which was biased at 380 keV) is associated with the isomeric state, while the remaining 7% is associated with the prompt transition to the stable ground state of $Pb^{207}$. The actual yield, corrected for branching, is therefore 0·194. The difference between the experimental and theoretical yields (0·194 and 0·227) is not considered significant since imperfect shielding of the effluent downstream from the resin could account for the observed difference.

In Fig. 7(b) the results obtained on eluting the same resin bed with 0·5 M HCl (containing no $Bi^{207}$) are shown. Rapid decrease of the counting-rate of the resin is observed, as before, during the period of rapid elution. On stopping the flow, the counting-rate rises to a new equilibrium value, 5% less than the original, indicating that 5% of the $Bi^{207}$ parent diffused out during the run. The low rate of removal of the strongly adsorbed bismuth parent at the flow-rate of the experiment indicates that the flow-rate was not sufficiently fast for removal of Bi(III) to be diffusion-controlled, or that the diffusion coefficient of the Bi(III) species in the resin is appreciably smaller than that of Pb(II). Further work to determine the diffusion coefficient of Bi(III) in the resin would elucidate this point. However, for present purposes, the diffusion coefficient of Bi(III) need not be known for the calculation of the yield for the $Pb^{207m}$ separation in the recirculating system.

From the above results the conclusion can be drawn that diffusion theory coupled with radioactive decay rate considerations can be used to estimate the yield for separations involving short-lived daughter activities. By the techniques described, ion-exchange separation of daughter elements having half-lives of the order of milliseconds should be possible when diffusion coefficients, distribution coefficients, and branching relationships of the parent and daughter species involved are favourable.

*Acknowledgement*—The authors are indebted to Dr. K. A. KRAUS for helpful discussions during the course of this work.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 243 to 247. Pergamon Press Ltd., London

# ION-EXCHANGE SEPARATIONS OF THE LANTHANIDES AND ACTINIDES BY ELUTION WITH AMMONIUM ALPHA-HYDROXY-ISOBUTYRATE*

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**Abstract**—Lanthanide and actinide separations by means of elution with ammonium α-hydroxy-isobutyrate solutions at room temperature from Dowex 50-X4 resin columns were investigated. Separations comparable to those reported[1, 2] for elution from Dowex 50-X12 resin columns with hot ammonium α-hydroxy-isobutyrate were obtained. The simplicity and convenience of the method recommend it for use on the tracer scale.

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## INTRODUCTION

Choppin and others[1, 2] have reported the use of hot (87°C) ammonium α-hydroxy-isobutyrate solutions for lanthanide and actinide separations, eluting them differentially from Dowex 50-X12 ion-exchange columns. An elevated temperature is required with the highly cross-linked resin in order to attain resin-solution equilibrium quickly. However, hot columns require specialized equipment and techniques, and become cumbersome when many samples must be prepared. Therefore, an investigation of the elution characteristics of actinides and lanthanides in tracer concentrations with this elutriant at room temperature (~25°C) with Dowex 50-X4 was made. The 4% cross-linked resin was chosen because of its apparent rapidity in attainment of equilibrium.

## EXPERIMENTAL

*Reagents and equipment.* Three different batches of alpha-hydroxy-isobutyric acid (2-carboxy-propanol-(2) were used for the experiments. These included a batch manufactured by Distillation Products Industries, Rochester, N.Y., one from Fairmount Chemical Company, Newark, N.J., and a preparation by the authors.[3, 4] The Dowex 50-X4 resin was obtained from BioRad Laboratories, Berkeley, California, and water graded to obtain the fraction settling at 0·5–1·5 cm/min. Drop counters Model DCC-2 (LASL design) were used to collect the fractions from the columns.

Resin columns of about 2-mm diameter and from 3·5 cm to 12 cm in length were used. The free-column volume (volume of liquid in the column) was determined by passing a drop of very dilute $HCl^{36}$ through the column and determining in which drop the activity first appeared. The free-column volume was approximately 0·6 of the apparent column volume.

*Column technique.* For the experiments, the lanthanide and actinide activities in 0·1 N HCl were equilibrated with a small drop of resin, centrifuged, and the liquid withdrawn. A water slurry of the resin in the ammonium form was then transferred onto the column, which had previously been washed with several volumes of the eluting solution to be used. The resin was allowed to settle, the water supernate withdrawn, and the column reservoir was rinsed with the elutriant. Elution was

* This work done under the auspices of the US Atomic Energy Commission.

[1] G. R. Choppin and R. J. Silva *J. Inorg. Nucl. Chem.* **3**, 153 (1956).
[2] G. R. Choppin, B. G. Harvey, and S. G. Thompson *J. Inorg. Nucl. Chem.* **2**, 66 (1956).
[3] K. N. Welch and G. R. Clemo *J. Chem. Soc.* 2629 (1928).
[4] H. G. Rule and J. Harrower *J. Chem. Soc.* 2325 (1930).

then begun at a rate of from 30 sec to 3 min per drop. The fractions were collected on platinum plates, counted for the appropriate activity, and plotted in order to determine the peak positions.

## RESULTS

The results of these elutions are plotted in Figs. 1 and 2. Fig. 1 shows the elution position in free-column volume units (minus the first free-column volume) versus pH for nearly constant molarity, 0·49 M (D.P.I. preparation*) and 0·50 M (Fairmount preparation) ammonium α-hydroxy-isobutyrate. A few points were also obtained at 1·0 and 0·2 M. In order to compare all of these, the anion activity at each pH and molarity was calculated in the usual manner:

$$K_i = \frac{(H^+)(A^-)}{(HA)} \sim \frac{10^{-pH}\,(A^-)}{(M_{HA}) - (A^-)}$$

or

$$(A^-) = \frac{K_i\,(M_{HA})}{10^{-pH} + K_i}$$

The ionization constants $K_i$ were determined by measuring the pH of various molarities of the acid. The reciprocal logarithms of the ionization constants, $pK_i$, are entered in Table 1. In the calculation of anion activities, the $K_i$ appropriate for each molarity was used.

Table 1. Ionization constants

| Molarity | pH | $pK_i$ |
|---|---|---|
| 0·01 | 3·03 | 4·02 |
| 0·10 | 2·50 | 3·99 |
| 0·20 | 2·34 | 3·97 |
| 0·25* | 2·31 | 4·01 |
| 0·50 | 2·12 | 3·93 |
| 1·00 | 1·95 | 3·90 |
| 2·00 | 1·75 | 3·80 |

A log-log plot of the elution position (minus the free-column volume) versus the anion activity is shown in Fig. 2. In the cases (Lu, Yb, Y, Eu, Pm) where several points have been obtained for a given element, nearly parallel straight lines seem to be formed. Similar lines have been constructed for most of the other elements even though sufficient data were not available to confirm the hypothesis. Points below 1 column volume were not considered reliable and were omitted from the plot. The results indicate systematic differences among eluting solutions prepared from the different batches of α-hydroxy-isobutyric acid. These observed trends may be due to varying amounts of water and other impurities in the original compound which result in errors in the calculation of the molarity-sensitive anion activities.

* Distillation Products Industries preparation. All other molarities are from a Fairmount Chemical Company preparation.

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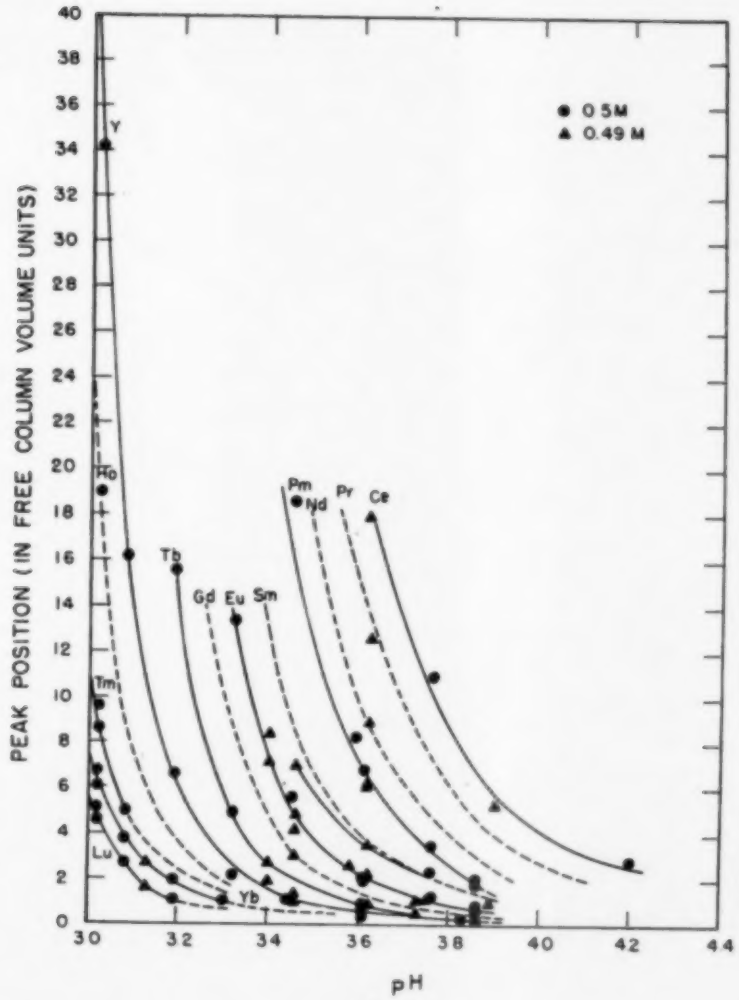


FIG. 1.

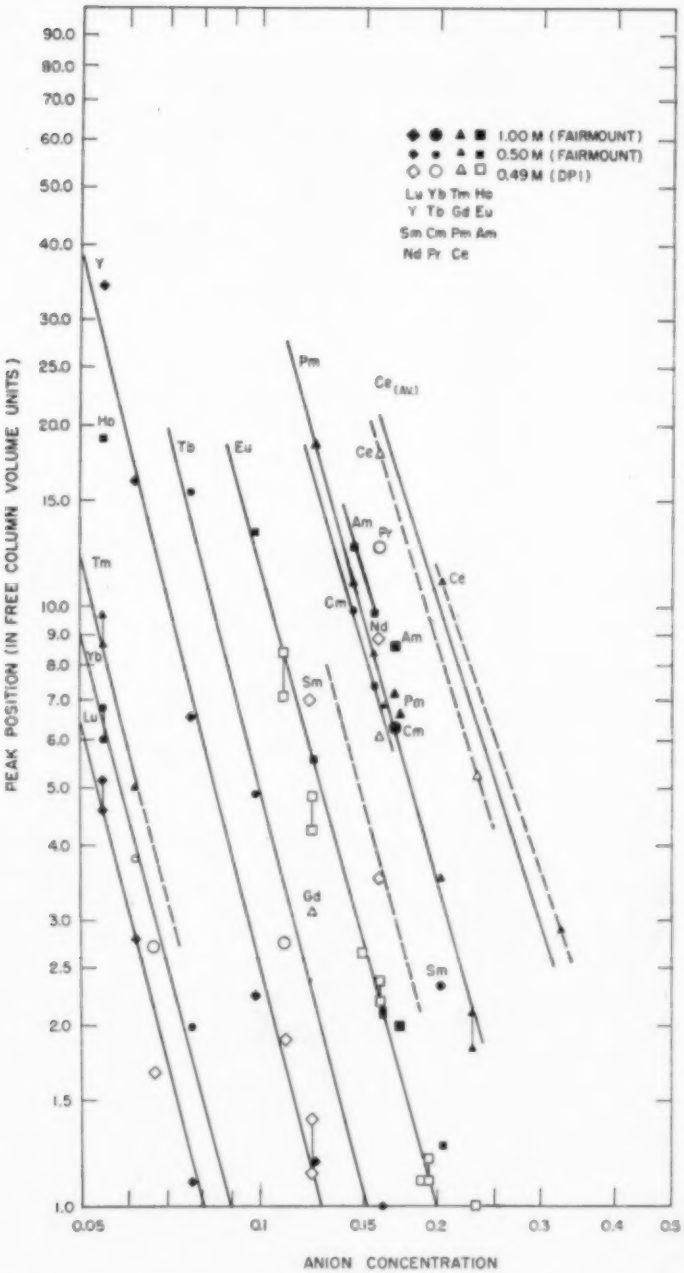
1.00 M (FAIRMOUNT)
0.50 M (FAIRMOUNT)
0.49 M (DP1)
Lu Yb Tm Ho
Y Tb Gd Eu
Sm Cm Pm Am
Nd Pr Ce
PEAK POSITION (IN FREE COLUMN VOLUME UNITS)
ANION CONCENTRATION
90.0
80.0
70.0
60.0
50.0
40.0
30.0
25.0
20.0
15.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.5
2.0
1.5
1.0
0.05
0.1
0.15
0.2
0.3
0.4
0.5
Y
Ho
Tm
Yb
Lu
Tb
Eu
Pm
Ce(AN)
Ce
Am
Pr
Cm
Nd
Sm
Gd

FIG. 2.

Table 2 summarizes the separation factors as indicated by the average relative peak positions, normalized to Cm = 1·00. Also tabulated for comparison are the relative peak positions obtained by CHOPPIN and SILVA.[1]

TABLE 2.—SEPARATION FACTORS WITH AMMONIUM α-HYDROXY-ISOBUTYRATE (Cm = 1·0)

| Element | LASL | UCRL[1] |
|---|---|---|
| Mv | — | 0·049 |
| Fm | — | 0·069 |
| E | 0·13 | 0·13 |
| Cf | 0·19 | 0·20 |
| Bk | 0·37 | 0·45 |
| Cm | 1·00 | 1·00 |
| Am | 1·39 | 1·4 |
| Lu | 0·011 | 0·015 |
| Yb | 0·016 | 0·020 |
| Tm | 0·022 | 0·026 |
| Er | — | 0·037 |
| Ho | 0·039 | 0·055 |
| Y | 0·069 | 0·06 |
| Dy | 0·076 | 0·078 |
| Tb | 0·14 | 0·14 |
| Gd | 0·22 | 0·28 |
| Eu | 0·34 | 0·39 |
| Sm | 0·7 | 0·71 |
| Pm | 1·1 | 1·2 |
| Nd | 2·3 | 2·1 |
| Ce | 3·4 | 3·5 |

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*Acknowledgements*—The authors wish to express their appreciation to Mrs. FRANCINE LAWRENCE for her invaluable assistance in preparation and counting of samples, to members of the University of California Radiation Laboratory at Berkeley, California, for isolation of the actinide fraction from a plutonium "napkin ring," to the MTR staff for the napkin-ring irradiation, and to the staff of the LASL "water boiler" for the rare-earth irradiations.

# LETTERS TO THE EDITORS

## Separation of Actinide Elements by Cation Exchange using Alpha-hydroxy isobutyric acid

(*Received* 16 *July* 1956)

By courtesy of the Editors, we have read the paper by H. L. Smith and D. C. Hoffman[1] in proof, and we feel that some confirmatory results obtained with an independently prepared reagent, and with a cation-exchange resin of British manufacture, may be of interest.

We have recently studied the separation of californium, curium, and americium by elution from a cation-exchange column with α-hydroxy isotubyric acid. The californium was prepared by carbon-ion bombardment of uranium in the Birmingham cyclotron.[2] The columns, 2 mm in bore and from 3 to 10 cm high were packed with Zeo-Karb 225 resin, graded to settle in water at from 0·2 to 0·5 cm per minute, and were operated at 77°C. The eluting solution was 0·4 M α-hydroxy isobutyric acid, adjusted to pH 4·0.

The separation factors are quoted in Table 1, on the same basis as those reported from Los Alamos[1] and Berkeley;[3] the elution volumes, after subtracting the free-column volume are expressed relative to the curium-elution volume. For comparison, the values reported by Smith and Hoffman[1] are given in parentheses.

Table 1

| Element | Relative elution volume | |
|---|---|---|
| Cf | 0·21 | (0·19) |
| Cm | 1·00 | (1·00) |
| Am | 1·38 | (1·39) |

We wish to acknowledge the co-operation of Dr. J. H. Fremlin and the cyclotron operating staff at Birmingham, and also Mrs. K. M. Glover for carrying out the α counting and pulse analysis of samples.

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*Harwell, Didcot, Berks*

[1] H. L. Smith and D. C. Hoffman *J. Inorg. Nucl. Chem.* **3**, 243 (1956).
[2] J. H. Fremlin, K. M. Glover, and J. Milsted *ibid.* **2**, 265 (1956).
[3] G. R. Choppin, B. G. Harvey, and S. G. Thompson *ibid.* **2**, 66 (1956).

## Formation of $Be^{10}$ from $B^{10}$

(*Received* 4 *May* 1956)

In the course of work on beryllium, attempts were made to prepare $Be^{10}$ sources of high specific activity from different materials. One of the results, though unsuitable for the intended purpose, merits reporting as a confirmation of the low cross-section of the reaction involved.

It is apparent that boron maintained in a reactor should contain $Be^{10}$ formed through $B^{10}(np)Be^{10}$. This process, the cross-section of which has been estimated to be about 3 millibarns for fast neutrons,[1]

[1] C. Eggler, D. J. Hughes, and C. M. Huddleston *Phys. Rev.* **74**, 1239(A) (1948).

appears to be exoergic to the extent of 0·25 MeV and should proceed, therefore, with thermal neutrons.

The direct irradiation of boric acid is unecomonic because of the competitive reaction $B^{10}(n\alpha)Li^7$, so the experiments were made with some boron carbide taken from an old BEPO shut-off rod obtained from Harwell. This is believed to have received not more than $6 \times 10^{17}$ n/cm$^2$, and possibly considerably less.

A mixture of 1·00 g of boron carbide with 5·0 mg of beryllium oxide (carrier) was treated, in different experiments, in the following ways: (1) fusion with sodium carbonate and sodium chlorate; (2) fusion with sodium hydroxide and sodium nitrate; (3) heating at 700°C in a current of chlorine. The resulting material was dissolved in dilute hydrochloric acid, most of the boric acid formed was filtered off after cooling, and the beryllium was separated following the MacMillan[2] procedure. The basic beryllium acetate obtained was purified by sublimation and conveniently transformed into beryllium oxide. This was weighed and its activity measured in a G-M thin-window counter at about 20% efficiency.

The results of the three experiments appear in Table 1.

TABLE 1.—YIELD OF BERYLLIUM ACTIVITY FROM 1·00 G OF BORON CARBIDE PLUS 5 MG OF BERYLLIUM OXIDE AS STARTING MATERIAL

| Experiment No. | BeO recovered (mg) | Activity (c.p.m.) | Sp. activity (c.p.m./mg) |
|---|---|---|---|
| 1 | 3·9 | 5·0 ± 1·1 | 1·29 ± 0·32 |
| 2 | 4·1 | 4·1 ± 1·0 | 1·00 ± 0·28 |
| 3 | 4·6 | 5·2 ± 1·7 | 1·13 ± 0·37 |

The specific activity was maintained after a repurification by the basic acetate procedure.

In a fourth experiment, 100 g of boron carbide and 20 mg of beryllium oxide were attacked as in experiment 2. The yield was 8·2 mg and the activity 186 ± 9 c.p.m., which corresponds to 22·7 ± 1·4 c.p.m./mg. This is equivalent to a value of 0·91 c.p.m./mg in the previous experiments. An aluminium absorption curve made with this sample gave $E_0 \sim 500$ keV, agreeing satisfactorily with the recorded value[3] of 556 keV for $Be^{10}$.

As there were no exact data on the irradiation conditions, no attempt was made to determine the counting efficiency and the original beryllium content of the boron carbide accurately. The second quantity, however, must be negligible, as comparison of results from experiments 2 and 4 shows. With this assumption, and with 20% as a rough figure for the counting efficiency, the $Be^{10}$ activity developed in the boron carbide is about 0·4-0·5 dps/g. This implies a thermal cross-section of >7 mb for the $B^{10}(np)Be^{10}$ reaction, which may be compared with fast cross-section of 3 mb of EGGLER *et al.*

The alternative explanations of the formation of $Be^{10}$ by fast neutrons on $C^{13}$ by $(n\alpha)$ or on some beryllium impurity by $Be^9(n\gamma)Be^{10}$, both reported by HUGHES *et al.*,[4] appear much less probable. The first would have required a much longer irradiation time, and the second a level of impurity not compatible with the agreement of experiments 2 and 4.

This work was performed at the Radiochemical Laboratory, The University Chemical Laboratories, Cambridge, England, under the direction of Dr. A. G. Maddock. It was carried out during tenure of scholarships from the Argentine Atomic Energy Commission, which are acknowledged.

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[2] E. M. MACMILLAN *Phys. Rev.* **72**, 591, 1947.
[3] F. AJZEMBERG and T. LAURITSEN *Rev. Mod. Phys.* **27**, 77 (1955).
[4] D. J. HUGHES, C. EGGLER and C. M. HUDDLESTON *Phys. Rev.* **71**, 269 (1947).

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## The Intermediate in the Preparation of Perchloryl Fluoride

(*Received* 10 *May* 1956)

An improved preparation of perchloryl fluoride from potassium perchlorate and fluorosulphonic acid has been described.[1] We wish to comment on the belief that dioxy-chloryl trisulphate $(ClO_2)_2S_2O_{10}$ is an intermediate in the reaction. If this is true the valency state of part of the chlorine in the perchlorate is reduced presumably by liberation of oxygen or oxidation of fluorosulphonic acid. The reaction can be explained without invoking a reduction mechanism. Previous work on ionization in fluorosulphonic acid[2] showed that fluorosulphonates and some fluorides behaved as bases in fluorosulphonic acid whilst other fluorides behaved as acids. Perchloric acid in fluorosulphonic acid, however, did not behave as an acid and an ionization of the type

$$2HSO_3F + HClO_4 \rightleftharpoons ClO_3^+ + 2SO_3F^- + H_3O^+$$

was postulated to explain the observations. Similarly an equilibrium

$$3HSO_3F + KClO_4 \rightleftharpoons ClO_3^+ + 3SO_3F^- + H_3O^+ + K^+$$

followed by thermal decomposition could lead to the formation of perchloryl fluoride.

The thermal decomposition of dioxy-chloryl trisulphate is not strictly comparable with its decomposition in solution. It has been shown[2] that sulphuric acid solutions in fluorosulphonic acid conduct as well as fluorosulphonates, and an equilibrium exists between sulphate and fluorosulphonate ions. Hence it is doubtful whether the trisulphate anion exists primarily as such in fluorosulphonic acid.

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[1] G. Barth-Wehrenalp *J. Inorg. Nucl. Chem.* **2**, 266 (1956).
[2] A. A. Woolf *J. Chem. Soc.* 433 (1955).

# BOOK REVIEWS

**The Metallurgy of Zirconium**, National Nuclear Energy Series, Division VII, Vol, 4. Edited by B. LUSTMAN and F. KERZE, McGraw-Hill Book Co. pp. 776. 75/-, $10.

A MODERN treatise on the extraction and application of a particular metal should not only contain a catalogue of the industrial methods which have been successfully applied to the production of the metal, but also should discuss the basic chemistry and physics which contributed to success. The book under review passes this test admirably, and as a result contains much which will be valuable to chemists, both academic and industrial.

Roughly half of the book is devoted to the chemical aspects of zirconium extraction and use, the rest describing the physical metallurgy of the melting, shaping, joining, and mechanical properties of this promising new material.

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About those sections of immediate interest to the chemist, it should be stated that the book covers a wide range of topics as thoroughly as possible at present, but these are largely presented in the context of the extraction and purification of zirconium. For example, the thermodynamic data all pertain to compounds which have been of interest so far in zirconium extraction, but this probably reflects the paucity of the chemist's effort in this direction rather than a deliberate selection.

The separation of hafnium from zirconium and the analytical procedures for the determination of many impurity elements in zirconium receive exhaustive treatment and these two chapters are certainly those of most immediate value to the chemist.

A long section is devoted to the corrosion of zirconium and some alloys. The word "corrosion" is used in its broadest sense not only to encompass aqueous-solution attack, but also the effects of gases at high temperatures. The thermodynamic, kinetic, and structural aspects of the latter type of corrosion appear to have reached an advanced state of knowledge.

The chapters on equilibrium diagrams and the extraction of the metal will probably be of more restricted interest to chemists. It is surprising, however, to find that some thirty odd diagrams can already be given in varying detail, although the dashed liquidus lines in nearly every one show how the container problem continues to bedevil this field. The chapter on extraction processes is very full from the point of view of facts and plant constructional details, but the lack of basic data makes any attempt at a fundamental description appear sterile. For example, the discussion of the iodide process would be more useful if any measurements of the free energies of formation of the iodides had been made.

The book is a commendable co-operative effort, brought up to date, and clearly adequate considering the title. It will be of direct value to chemists engaged in the zirconium industry, as well as being a source of useful ideas to others working on similar elements. For the less concerned chemist it contains a review of most of the established knowledge about zirconium, diluted heavily with more practical matters.

C. B. ALCOCK

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**Production of Heavy Water.** National Nuclear Energy Series. Division III, Volume 4F. Edited by GEORGE M. MURPHY, McGraw-Hill Book Company, 1955. pp. 394+xvii. 39/6, $5.25.

THE appearance of a second volume in the National Nuclear Energy Series of the US Atomic Energy Commission on the subject of heavy water, following the earlier volume by KIRCHENBAUM on heavy-water analysis, is an event to be welcomed. Much valuable information is given in Part I on the design and operation of the war-time distillation plants built in the USA and the chemical exchange plant built in conjunction with the existing electrolytic plant at the works of the Consolidated Mining and Smelting Company in Traill, BC, Canada. In Part II detailed information is given on chemical aspects of the various heavy-water processes investigated, and in particular on the development of suitable catalysts for the hydrogen-water exchange reaction. A number of alternative

exchange reactions of interest to chemists are also discussed, these including liquid-liquid exchange between isopropyl mercaptan and water, and a process involving alternate low-temperature hydrogenation of benzene followed by high-temperature dehydrogenation of the cyclohexane thus produced.

It must be admitted that some overlap is inevitable in a book of this character, which in reality comprises a collection of reports by various groups of workers. The work is also somewhat old, since it was carried out during 1940–1943 and was written up in the immediate post-war period. However, this delay was inevitable in view of the classification policy of the time. The USAEC must therefore be congratulated on making generally available such a large body of information, which it is to be hoped will have the desirable effect of directing the efforts of present-day workers in this field on to the most productive lines of research.

H. R. C. PRATT

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## ERRATUM

FRED FELIX and PIERRE JORDAN: Untersuchungen an heterogenen Systemen mit Hilfe von $Co^{60}$ als Indikator.

*J. Inorg. Nucl. Chem.* **3**, 125 (1956).

The legends are in the correct order but the illustrations above them, listed 1–11, should appear in the Fig. order 8, 9, 10, 11, 1, 2, 3, 4, 5, 6, 7.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 253 and 254. Pergamon Press Ltd., London

# SEARCH FOR $O^{20}$*

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(*Received* 17 *July* 1956)

**Abstract**—An attempt to detect $O^{20}$ prepared by an $(\alpha,2p)$ reaction on $O^{18}$ showed that the half-life of $O^{20}$ is not in the range 10 min to 150 years.

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THE potential utility of a radioactive isotope of oxygen with a half-life longer than that of $O^{15}$ (2 min) stimulated a search for $O^{20}$. Previous attempts to identify this isotope have not been successful.[1] From a rough estimate of the $O^{20}$ disintegration energy, it appeared that the half-life might be as long as 1 hour. The estimate is based on an extrapolation from the known masses [2, 3] of $Si^{32}$, $Mg^{28}$, and $Ne^{24}$, nuclei of the same type as $O^{20}$ ($Z$ even, $A = 2Z + 4$). The $Si^{32}$-$Mg^{28}$ mass difference is 3·9914 and the $Mg^{28}$-$Ne^{24}$ difference is 3·9915 mass units. By assuming the same mass difference for $Ne^{24}$-$O^{20}$, we obtain 20·0097 for the mass of $O^{20}$. Since the $F^{20}$ mass[2] is 20·0063, the disintegration energy of $O^{20}$ would be 3·2 MeV. Since the ground states of $O^{20}$ and $Ne^{20}$ are both $0^+$, and since it is known that the $F^{20}$-$Ne^{20}$ ground-state transition is forbidden,[4] we assume that the $O^{20}$-$F^{20}$ ground state transition is also forbidden. Therefore the predominant decay of $O^{20}$ is probably to the first excited state of $F^{20}$ at 0·65 MeV or to a higher level. If the 2·5 MeV transition to the first excited level is allowed, the half-life would be in the range 2–60 min. If the major transitions are to higher levels or if the transitions are forbidden, then an even longer half-life can be expected.

$O^{20}$ may be produced by an $\alpha,2p$ reaction in $O^{18}$. MgO, enriched in $O^{18}$ to 1·5%, was bombarded with 40-MeV $\alpha$ particles. Any $O^{20}$ found in the MgO target can be compared directly with $Mg^{28}$ produced [5]by the $\alpha,2p$ reaction on $Mg^{26}$. $O^{20}$ would decay to the known 11-sec $F^{20}$, which has one 1·63-MeV $\gamma$ ray per disintegration. Similarly, $Mg^{28}$ decays to 2·3-min $Al^{28}$ which has one 1·78-MeV $\gamma$ ray per disintegration. The ratio of $O^{20}$ to $Mg^{28}$ is obtained by comparing the intensities of these two $\gamma$ rays.

One gram of MgO was packed into a depression (4 in. × ½ in. × 1/16 in.) in a water-cooled Al block and covered with one mil Al foil. After a 280-$\mu$a-hr $\alpha$-particle irradiation, the MgO was dissolved in 10 ml 5·0 M HCl and distilled. The distillate was made basic with the minimum amount of solid NaOH, NaF holdback carrier was added, and the water was distilled. This distillation from basic solution was then repeated three more times. The last distillate (60% overall yield) was collected

* Research performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. K. SHELINE, E. C. CAMPBELL, and R. W. PEELE *ORNL* 1798 (December 1954).
[2] A. H. WAPSTRA *Physica* **21**, 367 (1955).
[3] B. J. DROPESKY and A. W. SCHARDT *Phys. Rev.* **102**, 426 (1956).
[4] C. WONG *Phys. Rev.* **95**, 765 (1954).
[5] R. K. SHELINE, N. R. JOHNSON, P. R. BELL, R. C. DAVIS, and F. K. MCGOWAN *Phys. Rev.* **94**, 1642 (1954).



1

3 hours after the end of the bombardment and placed on a 2 in. × 2 in. NaI(Tl) scintillator connected to a single-channel pulse-height analyser. Two aliquots of the Mg were purified, each dissolved in 6 ml of water and each counted under the same conditions as the purified $O^{20}$ water sample. The activity of the water sample was $<0{\cdot}8$ c/m in the 1·53–1·73-MeV channel, while the activity at the end of bombardment of the $Mg^{28}$ was $3{\cdot}6 \times 10^6$ c/m in the 1·68–1·88-MeV channel. All samples were corrected to 100% chemical yield. These data show that the half-life of $O^{20}$ must be greater than 150 years or less than 10 min if the $\alpha,2p$ cross-section on $O^{18}$ is $\geq 0{\cdot}1$ of the $\alpha,2p$ cross-section on $Mg^{26}$. The thick target cross-section for the latter reaction determined in this experiment is ~1 mb.

Gas-sweeping experiments were performed in an attempt to identify $O^{20}$ if its half-life were between 1 sec and 10 min. The target was 5-ml $H_2O$ (1·5% $O^{18}$) through which $O_2$ was bubbled at rates up to 6 litres/min. The gas was passed through one liquid-$O_2$ trap, two $CaF_2$ traps, and finally condensed to liquid oxygen. The activity in this liquid was measured with a NaI(Tl) scintillation spectrometer. No significant activities were observed other than 2-min $O^{15}$ and possibly 29-sec $O^{19}$. A preliminary experiment showed that ~25% of the $O^{15}$ was swept out of the target at flow rates of ~3 litres/min. These experiments indicate that if $O^{20}$ has a half-life between 1 sec and 10 min, the $(\alpha,2p)$ cross-section on $O^{18}$ must be less than a few millibarns. Since the corresponding $\alpha,2p$ cross-section on $Mg^{26}$ is known to be ~1 mb, there remains a good possibility that the half-life is in this range.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 255 to 262. Pergamon Press Ltd., London

# THE HAHN EMANATION TECHNIQUE USING TELLURIUM-IODINE-132

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(*Received* 18 *June* 1956)

**Abstract**—The emanation technique has been studied using iodine 132, which grows from tellurium 132, as the volatile component instead of the more usual radium-emanation system. Good agreement was obtained between the results, using iodine and emanation in a study of the heating of barium sulphate. When the method was applied to potassium and sodium sulphate, the results were less decisive.

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The "emanation method" for the study of changes in the solid state has required the use of the naturally occurring isotopes of radium and thorium which decay to form the inert gas, emanation. The rate of evolution of this has been used as a qualitative measure of reactions and rearrangements proceeding in the sample into which very small quantities of radium or thorium are uniformly incorporated. This latter condition is important and there must be many systems in which it is difficult to incorporate them satisfactorily. It seems appropriate, therefore, to consider what artificial radioactive elements decay to produce a volatile radioactive daughter product so that the labelling of a wider range of systems might become possible.

The desirable properties of such a radioactive system are a relatively long half-life for the parent so that decay during the experiment is not serious (which also simplifies the organization of supplies of the radioactive material in that frequent preparation of the source is not necessary), whilst the volatile daughter should have a short half-life so that radioactive equilibrium with the parent is rapidly attained when that equilibrium is seriously disturbed. If this does not occur within a short time compared with the time taken for large changes in emanating power to occur (e.g., on heating), then the rapid onset of a condition of high emanating power will result in a loss of most of the daughter which had accumulated in the solid. This subsequently causes an apparent fall in the emanating power as the reservoir of daughter product is depleted. This has been called the "Spitzen effect" by Zimens[1] and has been observed even with systems studied with thoron ($t_{\frac{1}{2}} = 54$ sec) as the volatile component.

A consideration was given to the known natural and artificial radioactive isotopes, but none satisfied the conditions apart from those originally used. Several rubidium and caesium isotopes decaying by positron emission or $K$ capture to inert gases are known, but the half-life or supply or both of the mother substances makes for difficulties; similarly, there are no halogen isotopes decaying to inert gases of half-

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[1] K. E. Zimens *Z. physik. Chem.* **191A**, 1 (1942).

life shorter than the parent, although Zimens[1] has used iodine-135 ($t_{\frac{1}{2}} = 6{\cdot}7$ hr) which decays to xenon ($t_{\frac{1}{2}} = 9{\cdot}3$ hr), to investigate, in a preliminary fashion, the changes occurring in silver iodide on heating. A pronounced peak in the emanating power of the solid occurred at 145°C, which agreed well with the value obtained using thorium X (radium-224) as the source of volatile component, but which was incorporated into the silver iodide probably by adsorption. This example, however, is not a very good one as the half-life of the parent is shorter than desirable and the calculation of emanating power, which Zimens discusses, is cumbersome because the half-lives are long compared to experimental times. Of other elements decaying to volatile daughter products, tellurium-132 seemed worthy of consideration. It has a half-life of 77 hours and produces iodine-132 (half-life of 2·26 hr) by $\beta$ decay. The growth of iodine-132 from its parent reaches a maximum at 12 hr, which is much longer than is desirable, but in view of the satisfactory results obtained with iodine–xenon-135 this fact is not of over-riding importance. Moreover, in crystalline systems which often are of low emanating power, small losses from the equilibrium amount of iodine in the solid would not materially affect the qualitative results obtained from a continuous record of the apparent emanating power in samples submitted to continuously changing temperature. The tellurium-iodine system is also of interest as its chemistry is very different from that of radium or thorium so that it might be used in systems where the latter would not be easily incorporated. A direct comparison of the tellurium-iodine system with that of radium-thoron is possible by means of barium sulphate, with which both form homogeneous systems, the radium replacing barium and the tellurium, as tellurate, the anion.

## EXPERIMENTAL

The use of tellurium-132 was investigated, using a continuous-flow system whereby the amount of iodine lost from the solid sample containing tellurium-132 to the gas stream could be measured continuously as the temperature was varied at a known rate. This method was used as being more powerful than the determination of emanating power at a range of fixed temperatures. Dry argon, metered by a conventional differential type flowmeter, entered at *A* (Fig. 1) at a rate of 200 cc/min and passed over the sample in the platinum boat *B*. When using argon, carbon dioxide, or nitrogen

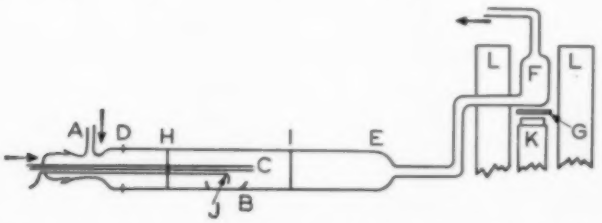


Fig. 1.—The apparatus. *A*, argon entry; *B*, sample boat; *C*, oxygen entry; *DE*, "Mullite" tube; *F*, measuring chamber; *G*, cooling coil for phosphor crystal; *HI*, main furnace; *J*, thermocouple; *K*, phosphor and detecting system; *L*, lead shield of detector system.

as the carrier gas, the bulk of the evolved iodine deposited on the walls of the "Mullite" tube (*DE*) and counting chamber (*F*). This effect was decreased by maintaining these parts at 200°C with a "Nichrome"-wound furnace. When oxygen was the carrier gas, however, there was no deposition. An inert gas is desirable to prevent any reaction with the sample under investigation so that oxygen was fed through the alumina tube *C* at a rate of 50 ml/minute and entered the argon stream approximately 2 cm beyond the sample boat *B*. Under these conditions less than 1% of the radioactive iodine was deposited in the measuring chamber *F*. The gas mixture carrying the evolved iodine-132

passed along the "Mullite" tube through the counting chamber *F* and was absorbed in a trap containing an alkaline solution of sodium bisulphite.

The passage of iodine-132 was detected by its $\gamma$-ray emission using a sodium iodide-thallium activated crystal scintillation counter. The phosphor *K* was separated from *F* by a spiral glass tube *G*, through which circulated cold water to protect the scintillation crystal from the heat of the furnace around chamber *F*. The counting chamber and detector were shielded by lead walls (2 in thick), *L*, from $\gamma$-radiation from the remainder of the apparatus. The pulses from the scintillation counter were amplified and fed into a counting-rate meter, from which an e.m.f. proportional to the counting rate was applied to the input of a two-channel pen recorder. The temperature of the sample was measured by a chromel-alumel thermocouple *J*, and the e.m.f. from this was applied to the other channel of the recorder. This system enabled a continuous record of temperature and $\gamma$-ray count rate due to vaporized iodine in chamber *F* to be obtained. The main platinum-wound furnace *HI* was controlled through a "Variac" transformer operated manually to give a uniform temperature rise of 5°C per minute.

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## PREPARATION OF SULPHATES FOR EMANATION STUDY

Carrier-free tellurium-132 was obtained by separation from the fission products of uranium[2] and was supplied in dilute sulphuric acid. The solution (containing usually about 2·5 mc of tellurium-132) was made slightly alkaline with sodium-hydroxide solution and oxidized with sodium peroxide to give the tellurate ion. Thesolution was then neutralized with sulphuric acid, and sufficient aqueous barium-chloride solution was added with stirring to precipitate all the sulphate, yielding about 4 g of barium sulphate. Approximately 3 g of this material was used in any one experiment. The effects of concentration of reagents, ageing, and drying of the barium sulphate on the evolution of iodine (after it had reached equilibrium with its parent) when heated at a rate of 5°C per minute were studied.

Approximately 3 g each of potassium and sodium sulphates were prepared by crystallization from a solution containing carrier-free tellurium-132 (2·5 mc) oxidized to tellurate. Both specimens were preheated at 800°C for 24 hours and cooled before investigation.

## RESULTS AND DISCUSSION

### (a) *Barium Sulphate*

The emanation of thoron and radon from barium sulphate has been previously studied,[3, 4, 5, 6] but only to temperatures up to 1100°C. HAHN[3] reported that, on preignited samples, low emanating powers were obtained up to 770°, when the evolution of emanation rose smoothly to 82% at 920°C. On samples dried at 110° the increase in emanating power started at much lower temperatures corresponding to the evolution of absorbed water,[7] but when the sample was reheated, the results agreed with those of the preignited precipitates. The temperature at which the increase of emanating power of preheated samples occurred corresponded to 0·56 of the melting point of barium sulphate in degrees absolute, and agrees well with the Tammann point.[8] BALAREW and KOLAROW[6] obtained similar results but also shewed that secondary variations could be obtained due to the thermal history of the samples.

Using barium sulphate labelled with tellurium-132 as tellurate, the reproducibility

[2] L. E. GLENDENIN *Radiochemical Studies—the Fission Products* (Paper 275) Ed. C. CORYELL and N. SUGARMAN, McGraw-Hill, New York (1951).
[3] O. HAHN *Applied Radiochemistry* Cornell University Press, NY (1936).
[4] H. MÜLLER *Z. physik. Chem.* **A149,** 257 (1930).
[5] R. JAGITSCH *Trans. Chalmers. Univ. Technol. Gothenburg* **11** (1942).
[6] D. BALEREW and N. KOLAROW *Kolloid Z.* **88,** 161 (1939).
[7] D. BALAREFF and G. KUNDILAROW *Z. anorg. Chem.* **162,** 344 (1927).
[8] G. TAMMANN and A. SWORKYKIN *Z. anorg. Chem.* **176,** 46 (1928).

of the first emanating-power-temperature curves of samples dried only at 110°C was not good. Barium sulphate was prepared by precipitation from 100 ml of solution; the precipitate was aged under the solution for 2 hours, and, after filtration, dried at 110°C for 18 hours. The prominent "peaks" for various samples were not consistent in position or relative magnitudes (Fig. 2). However, the cooling and

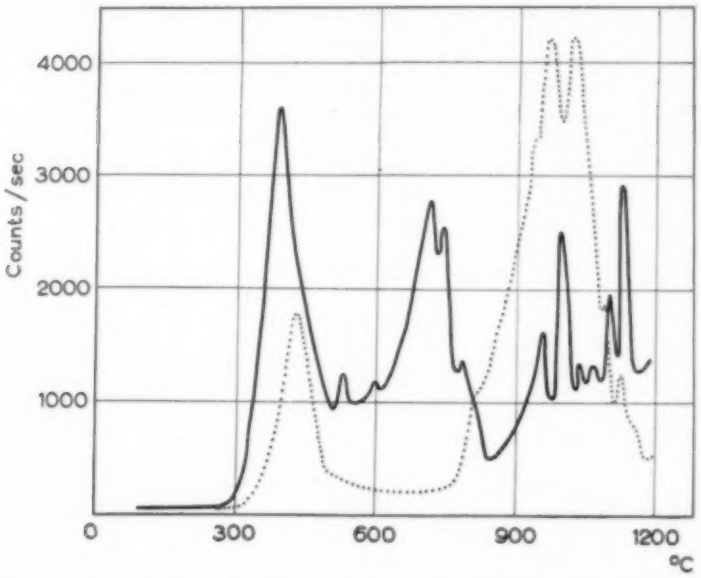


Fig. 2.—Emanation of iodine-132 against temperature for two different samples of barium sulphate prepared by an identical method and dried at 110°C. Rate of heating 5°C/min.

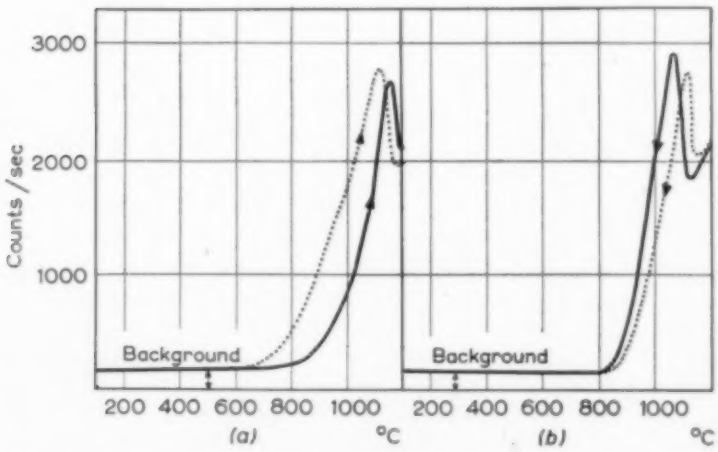


Fig. 3.—Emanation of iodine-132 against temperature for two different samples of identically prepared barium sulphate, preheated to 1200°C. (a) Heating curve, (b) cooling curve. Maxima for sample shown by dotted line, 1120°C (heating) and 1100°C (cooling). For sample shown by full line, the corresponding figures are 1160°C and 1075°C.

reheating curves showed good agreement (Fig. 3(b) and 3(a) respectively) although the temperature of the maximum varied a little.

The peaks obtained on first heating could be explained either by distillation of tellurium in addition to iodine-132 or to the escape of absorbed or occluded water (as has been observed with thorium hydroxide[9]) or possible annealing of the crystals. To test the first suggestion, the sample was heated in the usual way, but the counting chamber was maintained at room temperature, which allowed the volatile components to accumulate there during the experiment, and the radioactive decay of the $\beta$ activity was measured. The material however decayed completely with the half-life of iodine-132 ($t_{\frac{1}{2}} = 2{\cdot}26$ hr) with no evidence of the presence of tellurium 132 ($t_{\frac{1}{2}} = 77$ hr).

Attempts to determine the effects of occluded water were made by preparing barium sulphate under conditions which gave more perfect crystals than obtained by the conditions previously used. The occlusion of water is decreased by precipitation from very dilute solutions and preparations were accordingly made from 100 cc and 5, 10, and 20 litres of water, but no improvements in reproducibility of the curves were obtained. Similarly, variations in the times of ageing and drying (at low temperatures) were equally ineffective. This evidence, however, cannot exclude evolution of water vapour as the cause as we have no knowledge of the amount of water necessary to cause such effects. Losses of weight of 1% were found on heating to 450°C, and a further 1% in the region of 450°–800°C, in agreement with the thermo-gravimetric results of DUVAL.[10]

The irregular nature of the emanation of iodine in the first heating of barium sulphate dried at low temperatures is apparently inconsistent with the results of HAHN,[3] but his results were obtained (using radon) at a few fixed temperatures in the relevent temperature range, in which case the irregularities could have been missed. In all other cases, samples preheated to high temperatures were used.

After prior heating to high temperatures, the emanating temperature curves were reproducible. The temperature corresponding to the maximum in the heating curve varied between 1120°C and 1180°C from sample to sample on heating and between 1100°C and 1070°C on cooling compared with the transition known to take place in barium sulphate at 1149°C. Ignition of the precipitates for 24 hours at 1200°C did not materially alter the position of the peak obtained on cooling and on further heating. The peak cannot be due to a serious depletion of the store of iodine-132 in the solid (Spitzen effect) as the amount of iodine evolved per unit time at higher temperatures becomes greater than at the transition (this is not apparent in the two specimens shown in Fig. 3), and secondly the maximum is also obtained in the cooling curve. The hysteresis effect in the heating and cooling curves is found with many substances and has been explained by THOMAS and STAVELY[11] in terms of the free-energy relationships within a system undergoing a phase transition. It cannot be excluded also that the effect is an experimental one due to the rate of heating.

The temperature at which there was a marked increase in emanating power varied between 700°C and 870°C or between 0·53 and 0·62 of the absolute melting point and is in reasonable agreement with the values obtained by HAHN (700–800°C). These figures also agree with the "lattice-loosening temperature" of TAMMANN[8] which is

[9] O. HAHN and V. SENFTNER *Z. physik. Chem.* **A170**, 191 (1934).
[10] C. DUVAL *Inorganic Thermogracimetric Analysis*. Elsevier Publishing Co., New York (1953).
[11] D. G. THOMAS and L. A. K. STAVELEY *J. Chem. Soc.* 2572, (1951).

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between 0·5 and 0·6 of the melting point in degrees Kelvin. It is not certain by observation that the increased evolution of iodine is due to the phase change at 1149°C or to "lattice loosening." However, on plotting the logarithm of the amount of iodine evolved (in counts per second) against the reciprocal of the temperature in degrees Kelvin, a straight line was obtained up to 1000°C which suggests a single process. Since the process starts at a temperature well below the temperature of the phase change, the increased evolution is probably due to "lattice loosening."

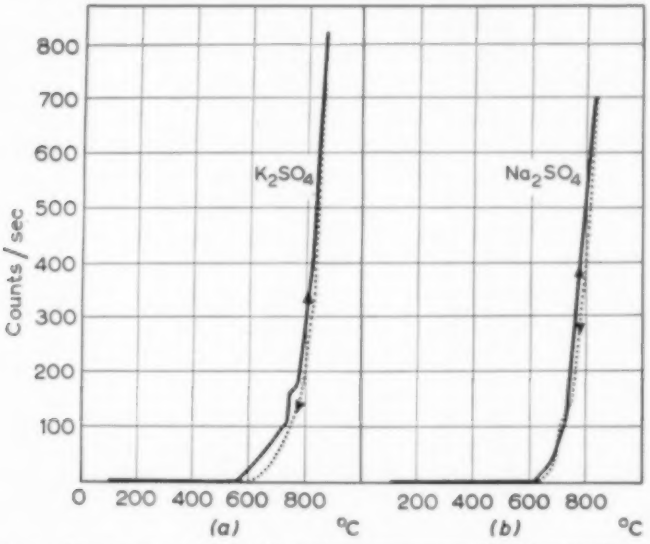


Fig. 4.—Emanation of iodine-132 against temperature for (a) potassium sulphate and (b) sodium sulphate. Both samples were preheated to 800°C.

Very similar results to those described using carrier-free material were obtained using tellurium with a specific activity of about 0·3 mc of tellurium-132 per milligram of tellurium element.

(b) *Potassium and Sodium Sulphate*

No previous work on emanating power of these salts has been reported. The temperature of the rhombic-hexagonal transition in potassium sulphate has been reported between 530°C and 610°C,[12, 13] Chatelier[14] for example obtaining values of 580°C on heating and 530°C on cooling. The melting point of potassium sulphate is 1349°K so that the "lattice-loosening temperature" at which the emanating power might be expected to increase would be 400°C to 535°C. We have not been able to detect the release of iodine from potassium sulphate below 560°C, above which there is a rapid increase in emanating power (Fig. 4a). On cooling, the release of detectable amounts of iodine does not occur at temperatures below 600°C. It is also apparent that there is no pronounced effect in the region of the temperature of the transition.

Somewhat similar results were obtained with anhydrous sodium sulphate (Fig. 4b)

[12] E. Mallard *Bull. Soc. Min.* **5**, 219 (1882).
[13] K. Huttner and G. Tammann *Z. anorg. Chem.* **43**, 215 (1905).
[14] C. Chatelier *Bull. Soc. Min.* **47**, 300 (1887).

in which there is a transition from a monoclinic to hexagonal form at 500°C and the Tammann region is 305°C to 421°C. There was no peak at the transition temperature and the visible rise in emanating power did not occur until 620°C (0·77 of the absolute temperature of the melting point).

With potassium sulphate, the increase in emanating power occurs at a temperature which is 0·62 of that of the melting point, and results as high as this were found for barium sulphate. It could also be argued that any effects of the phase transition in the region of 580°C is masked by the rapid increase in emanating power with temperature. No such explanation is possible, however, in the case of sodium sulphate, where the phase change occurs before there is any increase in emanating power due to "lattice loosening," the latter occuring at a much higher temperature than is usual. There are two possibilities which might account for these results, apart form the obvious one that the emanation of iodine is not a satisfactory indicator of changes of conditions in $Na_2SO_4$. The emanating power of the solid may be exceptionally low (due in part to crystal size) and is not visible until well above the Tammann region, although an undetectable increase may have taken place then, and at the transition temperature. This is supported by the observation that the emanating power was lower than anything else measured, and by the high value for the "lattice-loosening" temperature, which in many other systems is found as expected between 0·5 and 0·6 of the absolute melting point.

A second possibility is that the conditions were such that the transition effect was so small or took place so rapidly that it was unobservable. ZIMENS[16] has shown that the thermal history of a sample can change the emanating power at transitions, and he obtained the aragonite-calcite change at about 510°C without a "peak" by heating the aragonite at 490°C for one hour. BALAREW has obtained similar effects in other systems. In any case, the experimental assembly will tend to smooth a sharp peak because of diffusional and turbulent mixing in the gas phase between the sample and the detecting chamber (*B* and *F* in Fig. 1). The electronic and recording instruments also introduce some smoothing.[17]

## CONCLUSIONS

Three differences between the use of emanation and iodine as the volatile components can be expected. Firstly, the emission of radon is due to two physical reasons, gaseous diffusion from the crystal and recoil of the radon molecule from the surface layers when the parent molecule disintegrates by emission of an $\alpha$ particle. The latter mechanism is negligable for iodine-132 due to the much smaller recoil caused by the emission of a $\beta$ particle by tellurium-132. A second difference lies in the greater chemical reactivity of iodine compared with radon, the effects of which cannot be assessed here. Thirdly, iodine is much less volatile than radon and is absorbed more readily. This will limit the lowest temperature at which tellurium–iodine-132 can be used, and which may be of the order of room temperature or slightly above.

In spite of these differences, however, good agreement was obtained between results using emanation and those with iodine-132 in barium sulphate. The transition known to occur at 1149°C is clearly indicated. The results of the emanating-power

[15] G. WYROUBOFF *Bull. Soc. Min.* **13**, 311 (1900).
[16] K. E. ZIMENS *Z. physik. Chem.* **B37**, 231 (1937).
[17] J. N. GREGORY and J. HOWLETT A.E.R.E. Harwell, Report C/R 490. (1950).

experiments were qualitative only. Quantitative results are probably more easily obtained by conducting separate experiments at fixed temperatures. This would be relatively convenient as radioactive equilibrium between tellurium-132 and iodine-132 is established in 12 hours. It is assumed however, that all the iodine produced by $\beta$ decay is equally volatile. It is known[18] that, in solution, tellurium-132 as tellurate decays to iodine which is in the chemical forms of iodine, iodide and iodate, but the conditions in the solid state under heating are not necessarily similar.

*Acknowledgements*—We should like to thank Messrs. J. Eakins and S. Milsom (Isotope Division) for supplying tellurium-132 in its various forms, and Dr. J. Gregory for very useful discussions.

[18] W. H. Burgus and T. H. Davies *Radiochemical Studies—the Fission Products* (Paper 19) Ed. C. Coryell and N. Sugarman. McGraw-Hill, New York (1951).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 263 to 269. Pergamon Press Ltd., London

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# IONIZATION POTENTIALS AND THE CHEMICAL BINDING AND STRUCTURE OF SIMPLE INORGANIC CRYSTALLINE COMPOUNDS—I

## CHEMICAL BINDING

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(*Received* 17 *July* 1956)

**Abstract**—The differences in the bond character of simple inorganic crystalline compounds are considered in terms of ionic interaction. The ionization potentials $I$ of the electropositive constituents (first ionization potential for oxidation number + 1, second ionization potential for oxidation number + 2, etc.) are taken as a measure of the relative electrostatic field strengths of the respective cations. In the case of crystals regarded as formed through the interaction of cations of the same formal charge and similar (crystal) radius with a given anion, it is shown that the bonding appears to possess greater covalent character the greater the value of $I$. The variations in the nature of bonding with $I$ are correlated with lattice energies, interatomic distances, and colour, and also with magnetic, structural, and microwave data.

## INTRODUCTION

IN the interpretation of the problem of transitions between electrovalency and covalency, the concept of resonance between ionic and covalent structures and the principle of the electronegativity of elements are usually employed.[1, 2]

In the present paper the nature of bonding of metal–nonmetal crystals is considered from an ionic point of view. In this treatment it is assumed that, in the formation of crystals of inorganic salts, a hypothetical stage occurs, which involves interaction of the constituents as ions, whether the resulting compound is predominantly ionic or covalent. According to this approach, which is somewhat similar to that of FAJANS,[3, 4] it appears that only when cations exert a sufficiently large electrostatic field strength on their neighbours will a crystal lattice with bonds with covalent character be produced.

AHRENS[5] has suggested the use of ionization potentials $I$ (first for univalent cations, second for divalent cations, etc.) as a measure of the relative electrostatic field strengths of cations of the same formal charge in the formation of crystalline compounds.‡ One considerable advantage in using ionization-potential data is that accurate values are available for most of the cations with which we are concerned. Since the ionization potential is a measure of the energy required to remove a single electron from a free atom or ion, it is also a measure of the energy lost by the

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‡ GOLDSCHMIDT[6] in *Geochemistry* (Oxford, 1954) has suggested the use of values of ($I$/formal charge) as a measure of the polarizing force exerted by cations in crystals.

[1] L. PAULING *The Nature of the Chemical Bond*, Cornell (1940).
[2] C. A. COULSON *Proc. Roy. Soc.* **A207**, 63 (1951).
[3] K. FAJANS *Naturwiss.* **11**, 165 (1923).
[4] K. FAJANS and G. JOOS *Z. Physik.* **23**, 1 (1924).
[5] L. H. AHRENS *Geochim. et Cosmochim. Acta* **3**, 1 (1953).
[6] V. M. GOLDSCHMIDT *Geochemistry*, Oxford (1954).

recombination of the resulting ion and the electron, and hence may be taken as indicative of the attraction of the ion on the electron last removed. Although the ionization potential refers to free ions, it seems reasonable, when considering the formation of crystals from different cations of the same formal charge and (crystal) radius with a given anionic constituent, to employ the ionization potentials of the cations as an approximate comparative measure of their power of attraction for the most loosely bound electrons of the neighbouring anions. The greater the power of the cations for drawing the most loosely bound electrons of neighbouring anions to themselves, the greater the deviations from extreme ionic character that may be expected in the resultant crystal. According to this rather oversimplified picture, one might expect to observe transitions from essentially ionic towards essentially covalent character in crystalline compounds, regarded as initially formed from cations of the same formal charge and radius with a common anion, as the $I$ values of the cations become greater.

With regard to the comparison of the above ionic approach to bonding in crystals with the electronegativity concept of PAULING, it should be pointed out that his electronegativity values refer to stable equilibrium conditions, whereas the method which considers ionic interaction may be regarded as referring to a transitory stage governing the properties of the resulting crystal.*

## IONIZATION POTENTIALS AND TRANSITIONS BETWEEN ELECTROVALENCY AND COVALENCY IN SIMPLE INORGANIC CRYSTALLINE COMPOUNDS

In this section, some of the changes in bond character of crystalline compounds, regarded as initially formed from cations of the same formal charge and similar ionic (crystal) radii, are pointed out. Ideal comparisons are only possible when both the formal charge and size of the cations are equal, e.g. $Zr^{4+}$ ($r = 0{\cdot}79$ Å) and $Hf^{4+}$ ($r = 0{\cdot}78$ Å). In the present case, however, grouping has been carried out according to range of size, although radius differences must be taken into account in a detailed discussion.

In most cases it is not easy to ascribe to the bonding of inorganic crystalline compounds a definite amount of ionic or covalent character, and statements based on thermochemical electronegativity data such as ... "Beryllium bonds have the following amounts of ionic character: Be—F, 79%; Be—O, 63%; Be—Cl, 44%; Be—Br, 35%; Be—I, 22%" ...[1] can only be taken as giving a *rough* guide (see PRITCHARD and SKINNER[10]). For this reason, the transitions between electrovalency and covalency will be dealt with in a qualitative or semiquantitative way in this paper, and various properties which are widely regarded as giving indications of the ionic or covalent character of the compounds will be mentioned. Relations between ionization potentials and the different crystal structures are discussed in a second paper.

* In this connection, it is interesting to remember that MULLIKEN[7,8] has pointed out that the average of the *first* ionization potential and the electron affinity should measure the electronegativity of an atom. See BAUGHAN[9] and PRITCHARD and SKINNER[10] for a further discussion of this relationship.

[7] R. S. MULLIKEN *J. Chem. Phys.* **2**, 782 (1934).
[8] R. S. MULLIKEN *J. Chem. Phys.* **3**, 573 (1935).
[9] E. C. BAUGHAN *Quart. Reviews* **7**, 103 (1953).
[10] H. O. PRITCHARD and H. A. SKINNER *Chem. Reviews* **55**, 745 (1955).

TABLE 1.—UNIVALENT CATIONS. IONIZATION POTENTIALS AND RADII

| | $Cs^+$ | $Rb^+$ | $K^+$ | $Na^+$ | $Tl^+$ | $Ag^+$ | $Cu^+$ | $Au^+$ |
|---|---|---|---|---|---|---|---|---|
| $I$ (volts) | 3·893 | 4·176 | 4·339 | 5·138 | 6·106 | 7·574 | 7·724 | 9·223 |
| $r$ (Å) | 1·65 | 1·44 | 1·33 | 0·95 | 1·47 | 1·26 | 0·91 | 1·37 |

$I$ increases ⟶

*Crystalline compounds of univalent metals*

Table 1 shows univalent cations arranged in order of increasing first ionization potential of the corresponding atoms, together with their crystal radii.* For some purposes of comparison, $Na^+$ and $Cu^+$ should be omitted, and a more satisfactory sequence is obtained by considering only the larger cations $Rb^+$, $K^+$, $Tl^+$, $Ag^+$, and $Au^+$.

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A study of the properties of crystalline salts regarded as formed from the cations listed in Table 1 shows that a definite increase in covalent character occurs with increase in $I$. Thus when the $I$ value of the metallic element is less than *c.* 5·5 volts, not only the fluorides and chlorides but also the oxides, other halides, and sulphides are dominantly ionic anhydrous compounds. Thallium ($I = 6{\cdot}106$ V) in its univalent compounds begins to show definite deviation from truly ionic character, and shows chemical resemblances to its nearest large neighbours in Table 1—rubidium, potassium, and silver. Departure from extreme ionic behaviour is readily illustrated, for example, by the low melting-point (300°C) of the oxide $Tl_2O$. The thallous halides, however, are predominantly ionic in the crystalline state; this is suggested for TlCl by microwave data.[14] Silver, cuprous copper, and aurous gold compounds are more covalent in character, the only simple crystalline compound which is essentially ionic being silver fluoride.

The differences $\Delta$ between the values of the lattice energies of crystals calculated from experimental thermodynamic data ($U$) and theoretical values ($U_0$) calculated assuming ionic crystals with a van der Waals potential, have been used to give an indication of deviations from extreme ionic character. In Table 2 data are given on the experimental and theoretical lattice energies of univalent halides, according to the ionization potentials of the electropositive constituents. The remarkable agreement between values of $U$ and $U_0$ for the alkali halides provides strong support for the thesis that the forces operative in these crystals are those which underlie the theoretical calculations of $U_0$. The $\Delta$ values for TlCl, TlBr, and TlI suggest some departure from strict ionic character in these compounds. As the ionization potential of the cationic constituent becomes greater, as in the case of the argentous and cuprous halides, $U - U_0$ becomes more strongly positive, implying increased departure from strict heteropolarity. The lattice-energy data thus clearly indicate the trend for transitions from extreme ionic character to occur with increase in $I$.

* Ionization potential values employed throughout this paper are from FINKELNBURG and HUMBACH[11] and are in electron volts. Ionic radii are from AHRENS[12] as modified, with additions, after PAULING[1] and AHRENS[13].

[11] W. FINKELNBURG and W. HUMBACH *Naturwiss.* **42**, 35 (1955).
[13] L. H. AHRENS Unpublished data (1955).
[12] L. H. AHRENS *Geochim. et Cosmochim. Acta* **2**, 155 (1952).
[14] A. P. ALTSHULLER *J. Chem. Phys.* **22**, 1136 (1954).

Table 2.—Ionization potentials and the difference between lattice energies (kcal/mole) derived from experimental thermodynamic data and theoretical values for ionic crystals

| | Substance | $I$ (electropositive constituent) | $U$ | $U_0$ | $\Delta = U - U_0$ |
|---|---|---|---|---|---|
| | | V | | | |
| ← $I$ increases | CsF | 3·893 | 173 | 176 | −3 |
| | RbF | 4·176 | 185 | 183 | +2 |
| | KF | 4·339 | 195 | 193 | +2 |
| | NaF | 5·138 | 217 | 215 | +2 |
| | TlF | 6·106 | 198 | | |
| | AgF | 7·574 | 231 | 219 | +12 |
| | CuF | 7·724 | | | |
| | AuF | 9·223 | | | |
| | CsCl | 3·893 | 155 | 153 | +2 |
| | RbCl | 4·176 | 162 | 162 | 0 |
| ← $I$ increases | KCl | 4·339 | 171 | 168 | +3 |
| | NaCl | 5·138 | 185 | 184 | +1 |
| | TlCl | 6·106 | 176 | 167 | +9 |
| | AgCl | 7·574 | 219 | 203 | +16 |
| | CuCl | 7·724 | 234 | 216 | +18 |
| | AuCl | 9·223 | 249 | | |
| | CsBr | 3·893 | 151 | 150 | +1 |
| | RbBr | 4·176 | 157 | 156 | +1 |
| ← $I$ increases | KBr | 4·339 | 165 | 161 | +4 |
| | NaBr | 5·138 | 178 | 176 | +2 |
| | TlBr | 6·106 | 173 | 164 | +9 |
| | AgBr | 7·574 | 217 | 197 | +20 |
| | CuBr | 7·724 | 232 | 208 | +24 |
| | AuBr | 9·223 | 249 | | |
| | CsI | 3·893 | 143 | 143 | 0 |
| | RbI | 4·176 | 149 | 148 | +1 |
| ← $I$ increases | KI | 4·339 | 156 | 152 | +4 |
| | NaI | 5·138 | 167 | 164 | +3 |
| | TlI | 6·106 | 168 | 159 | +9 |
| | AgI | 7·574 | 214 | 190 | +24 |
| | CuI | 7·724 | 229 | 199 | +30 |
| | AuI | 9·223 | 251 | | |

$U$ values have a probable error of ±2–3 kcal, and have been calculated using the Born-Haber cycle from what is thought to be the best available thermodynamic data. It should be noted that these calculations employ values for the electron affinities of halogens from Pritchard[15], which are based on about ten independent experimental determinations. See Morris[16] for further details on the values for the alkali halides.

$U_0$ values for the alkali halides have been taken from Huggins,[17] for silver and thallous halides from Mayer,[18] and for cuprous halides from Mayer and Levy.[19] The values have a possible error of ±2–4 kcal even if the assumptions on which their calculation is based hold exactly.

[15] H. O. Pritchard *Chem. Reviews* **52**, 529 (1953).
[16] D. F. C. Morris *Acta Cryst.* **9**, 197 (1956).
[17] M. L. Huggins *J. Chem. Phys.* **5**, 143 (1937).
[18] J. E. Mayer *J. Chem. Phys.* **1**, 327 (1933).
[19] J. E. Mayer and R. B. Levy *J. Chem. Phys.* **1**, 647 (1933).

*Crystalline compounds of divalent metals*

Table 3 (a) and (b) shows divalent cations arranged in order of increasing second ionization potential of the corresponding atoms. The divalent ions are separated into two size groups. The division is arbitrary, but is based in part on the fact that the 6 : 3 rutile structure is common to the fluorides of the medium-sized group, whereas the 8 : 4 fluorite structure prevails in fluorides of the large-sized cations.

TABLE 3.—DIVALENT CATIONS: IONIZATION POTENTIALS AND CRYSTAL RADII

(a) Medium-sized ($r$ 0·6–0·9 Å) divalent cations

| | $Mg^{2+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ | $Pt^{2+}$ | $Pd^{2+}$ | $Cu^{2+}$ | $Ag^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $I$ (volts) | 15·03 | 15·64 | 16·18 | 17·05 | 17·96 | 18·15 | 18·54 | 19·42 | 20·29 | 21·48 |
| $r$ (Å) | 0·64 | 0·80 | 0·74 | 0·72 | 0·69 | 0·69 | 0·80 | 0·80 | 0·70 | 0·89 |

$I$ increases ⟶

(b) Large-sized ($r$ 0·95–1·35 Å) divalent cations

| | $Ba^{2+}$ | $Sr^{2+}$ | $Ca^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Hg^{2+}$ |
|---|---|---|---|---|---|---|
| $I$ (volts) | 10·00 | 11·026 | 11·87 | 15·03 | 16·904 | 18·751 |
| $r$ (Å) | 1·35 | 1·18 | 1·02 | 1·20 | 0·97 | 1·10 |

$I$ increases ⟶

Among the halides regarded as formed from the medium-sized divalent cations, those of magnesium appear to be predominantly ionic, although the bromide and iodide exhibit solubility in organic solvents. Interatomic-distance measurements and magnetic data* also suggest that all the halides of divalent manganese, iron, cobalt, and nickel have predominantly ionic character. In the case of the halides of divalent palladium ($I = 19{\cdot}2$ V), the crystalline substances $PdCl_2$ and $PdI_2$ are diamagnetic and can reasonably be regarded as possessing square essentially covalent bonds. From HUND's rules, the $Pd^{2+}$ ion should have two unpaired 4*d* electrons and should therefore have a magnetic moment of 2·83 BM calculated on the spin-only formula. If the bonding in the palladium halides was essentially ionic, therefore, they would be expected to be paramagnetic. In the case of the cupric and argentic

* It should be pointed out here that the interpretation of the magnetic criterion for bond type should be treated with some reserve. For example, PAULING[20] seems to have abandoned his original interpretation, and wrote in 1948:

"We conclude accordingly that the magnetic criterion distinguishes, not between essentially covalent bonds and essentially ionic bonds, but between strong covalent bonds, using good hybrid bond orbitals and with the possibility of unsynchronised ionic-covalent bonds, using poor bond orbitals, and the necessity for synchronisation of the covalent phases of the bonds."

While the precise meaning of PAULING's statement appears difficult to understand, some idea of the confusion on the subject may be gained by comparing the above statement with the account of MARTELL and CALVIN,[21] who point out some of the limitations of the magnetic method, but then conclude that, when the method may be applied, it indicates whether the bonds are "essentially covalent" or "essentially ionic." (See SELWOOD.[22])

[20] L. PAULING *J. Chem. Soc.*, 1461 (1948).
[21] A. E. MARTELL and M. CALVIN *Chemistry of the Metal Chelates*, Prentice-Hall, New York (1952).
[22] P. W. SELWOOD *Ann. Rev. Phys. Chem.* **4**, 445 (1953).

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halides, the magnetic criterion cannot be readily applied, since for both ionic and covalent configurations one unpaired electron may be expected. However, interatomic distance measurements and the crystal structure suggest that the bonding in cupric chloride crystals, for example, is essentially covalent.

Table 4.—Colour and covalency among crystalline compounds of large-sized divalent cations

| | Compound | Colour of crystals | Bond distance, Å | | |
|---|---|---|---|---|---|
| | | | Measured | Ionic radii sum (corrected where necessary) | |
| *I* increases ↓ | BaO | colourless | 2·75 | 2·75 | ionic character decreases → |
| | SrO | colourless | 2·54 | 2·53 | |
| | CaO | colourless | 2·40 | 2·39 | |
| | PbO | red, yellow | 2·30 | *c.* 2·6 | |
| | CdO | brown | 2·34 | 2·37 | |
| | HgO | red, yellow | | | |
| *I* increases ↓ | BaS | colourless | 3·18 | 3·19 | ionic character decreases → |
| | SrS | colourless | 3·00 | 2·97 | |
| | CaS | colourless | 2·83 | 2·83 | |
| | PbS | black | 2·96 | 3·04 | |
| | CdS | yellow | 2·51, 2·53 | 2·61 | |
| | HgS | red, black | 2·52, 2·91, 3·25 (red), 2·53 (black) | 2·94<br>2·73 | |
| *I* increases ↓ | $BaI_2$ | colourless | | | ionic character decreases → |
| | $SrI_2$ | colourless | | | |
| | $CaI_2$ | colourless | 3·12 | 3·15 | |
| | $PbI_2$ | yellow | 3.13 | | |
| | $CdI_2$ | brownish | 2·99 | 3·13 | |
| | $HgI_2$ | red, yellow | 2·78 (red) | 3·10 | |

Among the oxides regarded as formed from the medium-sized doubly-charged cations, magnesium oxide appears to be dominantly ionic, although X-ray studies have revealed that the ions in this compound, in contrast to those in sodium chloride, for example, are not entirely discrete.[23, 24] Ionic character is also evident in the oxides of ferrous iron ($I = 16{\cdot}18$ V) and cobaltous cobalt ($I = 17{\cdot}05$ V). Zinc oxide shows considerable deviation from ionic character, and the electron-density diagram shows that the electrons are not arranged symmetrically around the zinc and oxygen atoms as if they were in the ionic form, but there is an increased density between

[23] R. Brill, H. G. Grimm, C. Hermann, and C. Peters *Ann. Physik* **34**, 393 (1939).
[24] C. Peters *Z. Electrochem.* **46**, 436 (1940).

the zinc atom and the nearest oxygen atom of the irregular tetrahedral arrangement.[25, 26, 27] Nickelous oxide also shows deviations from ionic character and has a distorted structure below 200°C, while the oxides of divalent platinum, palladium, and copper are dominantly nonionic.

Among the monosulphides of the medium-sized divalent cations, essentially ionic character is shown up to manganese ($I = 15{\cdot}64$ V), and this appears to be the case with the disulphides also. Thus, for example, although $MnS_2$ and $FeS_2$ both have the pyrite structure, the available magnetic data for $MnS_2$, interpreted by the Weiss-Curie equation, leads to the value of 6·1 BM for the magnetic moment of manganese, in close agreement with the calculated spin moment of 5·92 BM for $Mn^{2+}$, whereas $FeS_2$ is only slightly paramagnetic and cannot correspond to an ionic structure, since the calculated spin moment of $Fe^{2+}$ is 4·90 BM.

Similar transitions from essentially ionic character to predominantly covalent character with increase in $I$ are shown in the compounds of the large-sized divalent cations of Table 3(b).

In many cases the increase in $I$ is accompanied by a deviation in the colours of the crystals from the colours of their components, which, according to PITZER and HILDEBRAND,[28] may be taken as an indication of covalency. An illustration of this effect is given in Table 4 by the colours of the oxides, sulphides, and iodides of the large-sized cations of Table 3(b).

The trend from typically ionic character towards covalency parallel to increasing ionization potential, which has been illustrated for compounds of univalent and divalent elements, is also observed in the crystalline compounds of elements forming cations of higher formal charge. When cations of a given oxidation number and range of size are considered, the levels of ionization potential at which considerable deviations from ionic character occur in crystals appear to depend largely upon the electron affinity and polarizability of the anionic constituent. Thus the fact that higher $I$ values are necessary to produce deviations from ionic character in the case of fluorides than with oxides, sulphides, and other halides may be correlated with the high electron affinity of fluorine and the low polarizability of the fluoride ion.

[25] H. J. YEARIAN *Phys. Rev.* **48**, 631 (1935).
[26] K. LARK-HOROWITZ and C. H. EHRHARDT *Phys. Rev.* **55**, 605 (1939).
[27] H. M. JAMES and V. A. JOHNSON *Phys. Rev.* **56**, 119 (1939).
[28] K. S. PITZER and J. H. HILDEBRAND *J. Amer. Chem. Soc.* **63**, 2472 (1941).

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J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 270 to 280. Pergamon Press Ltd., London

# IONIZATION POTENTIALS AND THE CHEMICAL BINDING AND STRUCTURE OF SIMPLE INORGANIC CRYSTALLINE COMPOUNDS—II

## CRYSTAL STRUCTURE

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**Abstract**—Inorganic crystalline compounds, whether structurally ionic or not, are considered as formed via an ionic stage. The structures are interpreted in the light of the properties of the interacting cations and anions. In the case of cations, the magnitude of their effective electrostatic field strengths is considered an important property. The importance of the polarizabilities of ions and their relative sizes in determining structures is also discussed. As a measure of the relative electrostatic field strengths of cations, ionization-potential values $I$ (first for univalent cations, second for divalent cations, etc.) are employed.

In the case of crystals regarded as formed through the interaction of cations of the same formal charge and similar (crystal) radius with a given anionic constituent, it is shown that there are certain threshold values of $I$ which serve to divide ionic from nonionic structures. Within the nonionic structure ranges there is evidence of fairly regular variations in structure with increase in ionization potential, until at very high $I$ values instability might result.

## INTRODUCTION

THE concept of a crystal being built up by packing of spheres, with the arrangement of ions in the crystal determined by radius ratio [$r$ (cation)/$r$ (anion)], has proved suitable for describing the structures of many simple inorganic compounds in which the bonding is predominantly ionic. In the case of crystalline compounds where the bonding is predominantly covalent in character, an explanation of the structures is commonly sought in terms of orbital hybridization.[1, 2, 3]

Although resonance-hybridization theory frequently seems able to predict structures successfully, exceptions are quite common. In addition, it is appropriate to point out that hybridization is only a convenient language, and to quote from COULSON[3] (p. 219):—

> "We must not, however, allow ourselves to believe that it (hybridization) represents any real phenomenon any more than resonance between different structures such as the covalent and ionic ones of a polar bond may be called a phenomenon."

In the present paper an attempt is made to explore another possible approach to the problem of nonionic structures (e.g. those not in accordance with the radius-ratio rules) of simple metal–nonmetal compounds. It is not our intention, however, to attempt to formulate a new theory or hypothesis, but merely to indicate possibly significant relationships which might ultimately be helpful for formulating a generally satisfactory theory. As in Part 1, it is assumed that the formation of simple inorganic crystalline compounds proceeds via an ionic stage, whether the resulting compounds

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† New College, Oxford.

[1] L. PAULING *The Nature of the Chemical Bond*, Cornell (1940).
[2] A. F. WELLS *Structural Inorganic Chemistry*, Oxford (1950).
[3] C. A. COULSON *Valence*, Oxford (1952).

are structurally ionic or not. Accordingly, the structure as well as the nature of the chemical bonding of the equilibrium product may be expected to depend, to some significant extent at least, on the properties of the interacting cation and anion. It will be assumed in accordance with the suggestions of FAJANS, WEYL, GOLDSCHMIDT, AHRENS[4] and others, that polarizability, particularly that of the anion, as it is usually more deformable than the cation, is an important property. For the cation the magnitude of its effective electrostatic field strength is considered the most important property, but other properties such as cation polarizability and a possible nonspherical charge distribution, even in the free cation, may also be significant. As before, the *n*th ionization potential ($I$) will be used as a measure for comparing the effective field strengths of cations of given formal charge ($n$) and (crystal) radius ($r$). It is easy, of course, to find several elements yielding cations of the same formal charge, but unfortunately not with precisely the same radius: consequently, elements will be grouped according to oxidation number and size magnitude, but the possibility that slight size variation may be important will not be overlooked.

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## CRYSTALLINE COMPOUNDS OF DIVALENT METALS

The compounds of elements forming medium-sized cations ($r = 0{\cdot}64$–$0{\cdot}90$ Å) are considered first.

The crystal energies of simple crystalline compounds, regarded as formed via such cations, are shown in Table 1, together with the second ionization potentials of the metallic constituents. The fact that the crystal energies fairly regularly increase with $I$ immediately suggests the possible importance of $I$ values in relation to crystal structure.* Indeed, it is found that the crystal structures of the compounds do vary fairly systematically according to the value of $I$.

The fluoride ion, with its small polarizability, appears able to withstand a powerful cationic field, and 6 : 3 ionic (rutile) structures are found among the fluorides formed from medium-sized divalent cations, even if $I$ is large. Rutile structures apparently

TABLE 1.—DIVALENT CATIONS: IONIZATION POTENTIALS AND CRYSTAL ENERGIES ($U$)
MEDIUM-SIZED ($r$ 0·6–0·9 Å) DIVALENT CATIONS

| | $Mg^{2+}$ | $Mn^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ | $Zn^{2+}$ | $Ni^{2+}$ | $Pt^{2+}$ | $Pd^{2+}$ | $Cu^{2+}$ | $Ag^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $I$ (volts) | 15·03 | 15·64 | 16·18 | 17·05 | 17·96 | 18·15 | 18·54 | 19·42 | 20·29 | 21·48 |
| $r$(Å) | 0·64 | 0·80 | 0·74 | 0·72 | 0·69 | 0·69 | 0·80 | 0·80 | 0·70 | 0·89 |
| $U$(MO) (kcal/mole) | 921 | 909 | | 957 | 963 | 973 | | 969 | 985 | |
| (MS) | 790 | 796 | 822α | 850($I$) | 858sph. 855wz. | 863 | | | 887 | |
| ($MF_2$) | 696 | 660 | 692 | 714 | 711 | 731 | | | 727 | 700 |
| ($MCl_2$) | 597 | 598 | 617 | 644 | 646 | 658 | | 661 | 661 | |
| ($MBr_2$) | 576 | 582 | 604 | 630 | 633 | 645 | | 649 | 645 | |
| ($MI_2$) | 550 | 563 | 586 | 611 | 617 | 623 | | | 632 | |

$I$ Increases ——→

* An even more regular relationship between the crystal energies and $I$ values is noted if compounds regarded as formed from cations of closely similar radius only are considered.

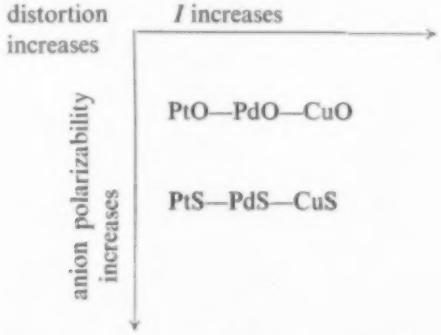
In this connection it should be pointed out that in the calculation of crystal energies by the Born-Haber cycle, the term generally of greatest numerical magnitude is the *total* ionization potential leading to the cation.

[4] L. H. AHRENS *Geochim. et Cosmochim. Acta* **3**, 1 (1953).

persist as far as Pd, although some distortion may be present. $CuF_2$ appears to have a related structure in which, however, the Cu-F distance is anomalously long. The structure of $AgF_2$ is not known, but is apparently complex. It seems that even $F^-$ is not able to withstand the extremely intense field of the very poorly shielded $Ag^{2+}$ ion. It is noteworthy also, that $AgF_2$ is the only stable simple salt of $Ag^{II}$, although stable complexes are known.

In the oxides of Table 1, ionic (NaCl) structures persist up to $I = c.$ 18 V, beyond which structures are nonionic. The break is not smooth, because whereas zinc is tetrahedrally co-ordinated in ZnO, the structure of NiO has 6 : 6 co-ordination; however, the structure of the latter oxide is free from distortion only above 200°C. Square planar co-ordination is found in PtO, PdO, and CuO ($I$ varies from 18·5 to 20·3 V). The oxygen arrangement is most nearly that of a perfect square in PtO, and distortion increases in the sequence PtO—PdO—CuO; that is with increase in $I$.

The sulphide ion $S^{2-}$ is more easily deformed than either $F^-$ or $O^{2-}$, and a change to nonionic structures begins at a distinctly lower value of $I$ than in the fluorides and oxides. The threshold value seems to be $c.$ 15·6 V ($I$ for Mn), beyond which only nonionic structures are found. MnS* itself is trimorphic, one form having 6 : 6 co-ordination and two others 4 : 4 co-ordination. FeS and CoS have the 6 : 3 NiAs structure, while ZnS has two dimorphic forms, sphalerite and wurtzite, each with 4 : 4 co-ordination. NiS is dimorphic, having a peculiar 5 : 5 (millerite) structure and also forming the NiAs structure. It seems that $Ni^{II}$ may be located at a threshold value, because if $I$ is increased much beyond 18 V only planar structures are found, as in PtS, PdS, and CuS; AgS is unstable. Moreover, although co-ordination of nickel is not of this type in either dimorph of the sulphide, square planar co-ordination has been reported in the mineral braggite (Ni, Pt, Pd)S, where $Ni^{II}$ is apparently able to assume this co-ordination (square planar co-ordination of S about $Ni^{II}$ may also be found in some complexes, e.g. potassium nickel dithio-oxalate).[5] In the sequence PtS—PdS—CuS, distortion is considerable in the first member, increases in PdS, while in CuS (covellite) a triangle of S atoms replaces the square as nearest neighbours. In the pairs PtO—PtS and PdO—PdS, distortion is greater in the sulphide than in the oxide, whereas in the pair CuO—CuS, only the oxide has planar (distorted) 4 : 4 co-ordination. These developments, together with those in the sequence PtO—PdO—CuO, may be summarized as follows;




* Polymorphism in MnSe is similar to MnS. MnTe has, however, the NiAs structure, as have FeS, CoS and one of the NiS dimorphs.

[5] E. G. COX, W. WARDLAW, and K. C. WEBSTER *J. Chem. Soc.* 1475 (1935).

In chalcopyrite ($CuFeS_2$), co-ordination of both Cu and Fe is tetrahedral and unlike that in the simple sulphides CuS and FeS. It has been noted[5] that the second ionization potentials of Cu and Fe average at *c.* 18 V, that is, very close to the second ionization potential of Zn; if the average field due to $Cu^{2+}$ and $Fe^{2+}$ has been a significant contribution in determining the co-ordination of $CuFeS_2$, its structure could be regarded as a compromise structure.

When bonded to radicals ($PO_4^{3-}$; $SO_4^{2-}$; $VO_4^{3-}$, etc.), ionic co-ordination is found to persist—at least in one compound of this type—all the way from Mg up to and including Cu; $H_2O$ may, however, have to be present in the structure as in $CuSO_4 \cdot H_2O$. Evidently the central atom ($P^V$, $V^V$, $S^{VI}$, etc.) in these radicals binds the oxygen-charge distribution firmly in the radical which is consequently able to withstand the effect of intense cationic fields even with ions such as $Cu^{2+}$; see also GOLDSCHMIDT[6] on contrapolarization. Some of the observations referred to above are summarized in Table 2. Arrows in Table 2 indicate the approximate range of ionic co-ordination for given anionic partners.

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*Compounds regarded as derived from large divalent cations*

$(r > c.\ 0{\cdot}95\ \text{Å})$

The crystal energies of simple crystalline compounds regarded as formed via such cations are shown in Table 3. As in Table 1, crystal energy varies fairly regularly with *I*.

(1) *Halides*

Two significant features about the structures of the halides of the large divalent cations may be noted:

(i) All fluorides, including that of very poorly shielded $Hg^{II}$, have the 8 : 4 fluorite structure.* This accords with the radius-ratio rule predictions.

(ii) None of the heavy halides of the large divalent cations has the 8 : 4 fluorite structure. This comes as a surprise, as some compounds, particularly $BaCl_2$, would be expected to have this structure. A variety of structures is in fact found: the 9-co-ordinated $PbCl_2$ structure; distorted 6 : 3 (rutile); $CdCl_2$ and $CdCI_2$ layer-type structures; and ZnS. Evidently the structures of the heavy halides of the large divalent cations are particularly sensitive to such properties as polarizability, cation-anion size relationship, and the effective field of the cation. The apparent significance of these properties may be gauged by examining structural relationships in various groups of halides. In Table 4 cation type is kept as uniform as possible by considering alkaline earths only. According to a suggested definition (AHRENS[7]) shielding efficiency is high and about equal in these species. Radius of cation varies considerably, as do the radii and polarizabilities of the anionic halide partners.

The developments in Table 4 may be compared with those in Table 5. Here one cationic species only is considered, namely $Hg^{2+}$, in which shielding efficiency is regarded as extremely low (AHRENS[8]), and accordingly the effective field of attraction

* $PbF_2$ is actually dimorphic (fluorite and $PbCl_2$ structures—WYCKOFF[7]).

[6] V. M. GOLDSCHMIDT *Geochemistry*, Oxford (1954).
[7] R. W. G. WYCKOFF *Crystal Structures*, Interscience, New York. (1951).
[8] L. H. AHRENS *Nature* **174**, 644 (1954).

TABLE 2.—CRYSTAL STRUCTURES AND APPROXIMATE RANGES OF IONIC CO-ORDINATION IN SULPHIDES, OXIDES, AND FLUORIDES OF ELEMENTS WHICH FORM MEDIUM-SIZED DIVALENT CATIONS

$I$ increases →

| $M^{2+}$ | Mg | Mn | Fe | Co | Zn | Ni | Pt | Pd | Cu | Ag |
|---|---|---|---|---|---|---|---|---|---|---|
| Sulphides | NaCl | NaCl, ZnS, ZnO (15·6) | NiAs | NiAs | ZnS, ZnO | 5 : 5 millerite, NiAs | coplanar | coplanar | distorted | unstable |
| Oxides | NaCl | NaCl | NaCl | NaCl | ZnO (*c.* 18) | distorted NaCl | coplanar | coplanar | coplanar | unstable |
| Fluorides | rutile | rutile | rutile | rutile | rutile | rutile | rutile? | rutile? (*c.* 19·5) | fluorite? | ? |
| Compounds with some polyatomic radicals, some with $H_2O$ | | | | | | | | | (20·3) | |

TABLE 3.—DIVALENT CATIONS: IONIZATION POTENTIALS AND CRYSTAL ENERGIES ($U$)

LARGE-SIZED ($r$ 0·95–1·35 Å) DIVALENT CATIONS

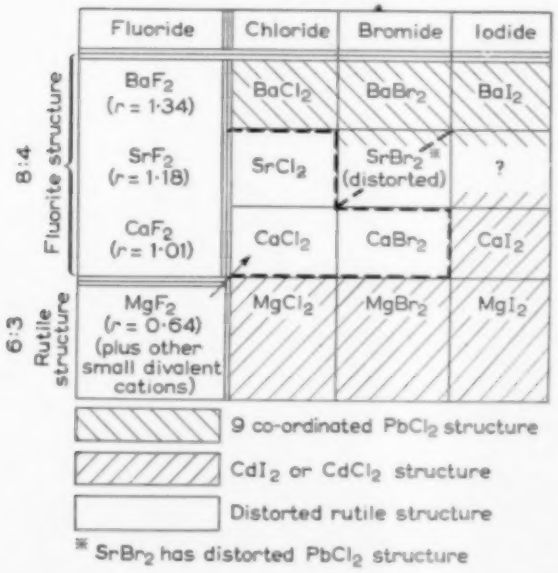
| | $Ba^{2+}$ | $Sr^{2+}$ | $Ca^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Hg^{2+}$ |
|---|---|---|---|---|---|---|
| $I$ (volts) | 10·00 | 11·026 | 11·87 | 15·03 | 16·904 | 18·75 |
| $r$ (Å) | 1·35 | 1·18 | 1·02 | 1·20 | 0·97 | 1·10 |
| $U$ (MO) (kcal/mole) | 744 | 784 | 831 | 834 red<br>834 yellow | 903 | 926 red<br>926 yellow |
| (MS) | 647 | 681 | 724 | 734 | 807 | 848 cinnabar<br>847 metacin. |
| ($MF_2$) | 553 | 589 | 624 | 596 | 662 | 655 |
| ($MCl_2$) | 483 | 507 | 535 | 534 | 602 | 626 |
| ($MBr_2$) | 466 | 489 | 515 | 523 | 592 | 620 |
| ($MI_2$) | 442 | 465 | 493 | 511 | 577 | 617 red<br>616 yellow |

$I$ increases ⟶

$U$ values have been calculated from experimental thermodynamic data, and refer to 25°C.

TABLE 4.—STRUCTURES OF ALKALINE EARTH HALIDES

($r$ = radius of cation)




is extremely high for a cation of this size and charge. The vertical arrangement of compounds is in order of decreasing polarizability of the anion ($F < Cl < Br < I$). It should be recalled that co-ordination predicted from ionic-radius ratio rules is 8 : 4 (fluorite). The fluoride structure is ionic, but those of $HgCl_2$, $HgBr_2$, and $HgI_2$ (yellow), though ionic in so far that octahedral co-ordination may be recognized, are

TABLE 5.—STRUCTURE-TYPE AND INTERNUCLEAR DISTANCES IN MERCURIC HALIDES

| Salt | Structure type | Internuclear distances (metal–nonmetal) |
|---|---|---|
| $HgF_2$ | fluorite | Hg {8 equidistant *F* atoms at 2·40 Å |
| $HgCl_2$ | distorted octahedral | Hg {2Cl 2·25 Å; 2Cl 3·34; 2Cl 3·63 |
| $HgBr_2$ | distorted octahedral | Hg {2Br 2·48 Å; 4Br 3·23 |
| $HgI_2$ (yellow) | distorted octahedral | Hg {2I 2·78 Å; 4I 4·11 |
| $HgI_2$ (red) | tetrahedral | Hg {4 equidistant *I* atoms at 2·78 Å |

severely distorted[2] and in a sense could be regarded as transitional. In this respect the dimorphs $HgI_2$ (yellow)–$HgI_2$ (red) are of unusual interest, and the relationship may be compared with that of polymorphic MnS (Table 2) and of dimorphic HgS (see below). The Hg-I distances of the four tetrahedral neighbours in red $HgI_2$ are equal to those with the two nearest iodines of the distorted octahedron in yellow $HgI_2$.

WELLS[2] (p. 116) has pointed out that the distorted octrahedral structure of $HgBr_2$ may be considered as in between a layer ($CdCl_2$ or $CdI_2$) and a molecular structure, and this observation is of particular interest when the structural changes in the halides of the divalent metals, as arranged below, are considered.

| | | | | |
|---|---|---|---|---|
| | $Ca^{2+}$ ($r = 1{\cdot}02$ Å) | $CaF_2$ (fluorite) | $CaCl_2$, $CaBr_2$ (deformed rutile) | $CaI_2$ ($CdI_2$ layer structure) |
| *I* increases ↓ | $Cd^{2+}$ ($r = 0{\cdot}97$ Å) | $CdF_2$ (fluorite) | $CdCl_2$, $CdBr_2$ ($CdCl_2$ layer structure) | $CdI_2$ ($CdI_2$ layer structure) |
| | $Hg^{2+}$ ($r = 1{\cdot}12$ Å) | $HgF_2$ (fluorite) | $HgCl_2$, $HgBr_2$ $HgI_2$ (yellow) (distorted octahedral) | $HgI_2$ (red) (tetrahedral) |
| *I* increases ↓ | $Sr^{2+}$ ($r = 1{\cdot}18$ Å) | $SrF_2$ (fluorite) | $SrCl_2$, $SrBr_2$ (distorted rutile) | $SrI_2$ (structure unknown) |
| | $Pb^{2+}$ ($r = 1{\cdot}20$ Å) | $PbF_2$ (fluorite and $PbCl_2$ structure) | $PbCl_2$, $PbBr_2$ ($PbCl_2$ structure) | $PbI_2$ ($CdI_2$ layer structure) |

It may seem a little surprising that most of the heavy halides of mercury are structurally ionic, albeit co-ordination is distorted, and this aspect is considered in a little detail below in the discussion on the oxides and sulphides of the divalent metals with large cationic radii.

TABLE 6.—STRUCTURES OF SIMPLE CRYSTALLINE COMPOUNDS OF UNIVALENT METALS

| | Cation | $r$ | Fluorides MF | Chlorides MCl | Bromides MBr | Iodides MI | Oxides $M_2O$ | Sulphides $M_2S$ |
|---|---|---|---|---|---|---|---|---|
| $I$ increases ↓ | $Cs^+$ | 1·65 Å | NaCl | CsCl | CsCl | CsCl | $CdCl_2$ | complicated |
| | $Rb^+$ | 1·44 | NaCl | NaCl | NaCl | NaCl | $CaF_2$ | $CaF_2$ |
| | $K^+$ | 1·33 | NaCl | NaCl | NaCl | NaCl | $CaF_2$ | $CaF_2$ |
| | $Na^+$ | 0·95 | NaCl | NaCl | NaCl | NaCl | $CaF_2$ | $CaF_2$ |
| | $Tl^+$ | 1·47 | distorted NaCl | CsCl | CsCl | CsCl | | complicated |
| | $Ag^+$ | 1·26 | NaCl | NaCl | NaCl | ZnS, ZnO | $Cu_2O$ | acanthite (low) |
| | $Cu^+$ | 0·91 | ZnS | ZnS | ZnS | ZnS | $Cu_2O$ | orthorhombic (low) |
| | $Au^+$ | 1·37 | | | | | | |

For details of these structures, see WYCKOFF[7]

*Structures of sulphides of metals which form large divalent cations*

Sulphides are listed below, the horizontal arrangement being in order of increasing second ionization potential of the electropositive constituents. Ionic radii of the corresponding cations are also given.

| | $I$ increases ⟶ | | | | | | |
|---|---|---|---|---|---|---|---|
| | BaS | SrS | CaS | SnS | PbS | CdS | HgS |
| $r$ (Å) | 1·35 | 1·18 | 1·02 | 0·93 | 1·20 | 0·97 | 1·10 |

BaS, SrS, and CaS have ionic (NaCl) structures. SnS has a distorted NaCl structure and PbS has the NaCl arrangement, whereas co-ordination in CdS is non-ionic (tetrahedral). As already noted, HgS is dimorphic, co-ordination in the black variety (metacinnabarite) is tetrahedral whereas that in the red (cinnabar) is octahedral.

The presence of ionic co-ordination in cinnabar, albeit distorted, and in PbS (galena), may be due to the large size of the $Hg^{2+}$ and $Pb^{2+}$ ions. It seems otherwise surprising that as co-ordination in CdS is tetrahedral, that in cinnabar could turn out to be octahedral, because as far as it can be ascertained, the effective field associated with $Hg^{2+}$ is considerably greater than that of $Cd^{2+}$. The inference is that, had the $Hg^{2+}$ radius been slightly smaller, say 1·05 Å as compared with the estimated 1·10 Å, only tetrahedral co-ordination would obtain in HgS, as is found in metacinnabarite. The presence of ionic co-ordination in galena can perhaps be interpreted in the same way. It may be assumed, as before, that reaction to form PbS proceeds via ions ($Pb^{2+}$ and $S^{2-}$) and that because the effective force of attraction associated with $Pb^{2+}$ is quite high—as compared with $Sr^{2+}$ of similar size, for example—the charge distribution about $S^{2-}$ is seriously deformed or polarized. The resultant PbS is consequently described as predominantly covalent rather than ionic, but, because $Pb^{2+}$ is very large, a complete rearrangement of electron distribution, involving a collapse to lower nonionic co-ordination, is prevented from taking place.

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Although co-ordination in PbS is not seriously deformed, that in $PbSnS_2$ (teallite) is distorted and similar to that in SnS. This relationship differs from that in the non-ionic sulphides CuS, FeS, $CuFeS_2$, and ZnS referred to above. Pb and Sn have fairly similar *I* values compared with Cu and Fe, where the values are quite widely different. If the average field of the two metal ions is important for determining the co-ordination in a compound with two electropositive constituents (see p. 273), it can be readily understood why the co-ordination in the compromise structure of $PbSnS_2$ should resemble that of SnS and PbS, whereas the compromise structure of $CuFeS_2$ bears little resemblance to the structures of CuS and FeS.

*Crystalline compounds of univalent metals*

The structures of simple compounds of univalent metals are shown in Table 6 in order of first ionization potential of the metal constituents.

Changes of structure with increase in *I* cannot be examined quite so critically in compounds of the univalent elements, because univalent cations are relatively easily polarized and this property may also influence structure (see below). Nevertheless, in general terms, we may observe that structure usually changes from ionic to non-ionic with increase in *I* (and with increase in the polarizability of the anion). Gold is particularly interesting in this respect. As defined,[8] the shielding efficiency of the Au core in $Au^+$ is lower than in any other univalent cationic core and hence the effective field strength associated with $Au^+$ is very great indeed. This may be a reason why no simple $Au^I$ compound is structurally ionic; the most likely possibility, AuF, is apparently not well characterized. (Extremely inefficient shielding in gold seems to account plausibly for some of the unusual chemistry of this element—extreme inertness, low atomic volume, extreme tendency to form complexes in solution, complete absence of structurally ionic compounds, and so on).

## $RO_2$ STRUCTURES

Co-ordination in the oxides of the quadrivalent elements invariably conforms quite closely to that predicted by the radius-ratio rules. There is some evidence, however, that the effective field of the cation might influence structure. Consider the following sequence of $M^{4+}$ cations, arranged in order of increasing radius—

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | ... $Mo^{4+}$, | $Sn^{4+}$, | $Nb^{4+}$, | $Hf^{4+}$, | $Zr^{4+}$, | $Pb^{4+}$, | $Am^{4+}$, | $Ce^{4+}$, $U^{4+}$ ... |
| radius (Å) | (0·70) | (0·71) | (0.74) | (0.79) | (0·79) | (0·85) | (0·92) | (0·94) (0·97). |

The oxides of cations with radii *c.* 0·70 Å have 6 : 3 (rutile) co-ordination, whereas oxides of the large cations have the 8 : 4 fluorite structure. The trio Hf—Zr—Pb are in a sense located in a transition zone. In the pair $HfO_2$—$ZrO_2$, the first component has the fluorite structure, whereas $ZrO_2$ has a distorted structure at room temperature and forms the fluorite structure only at elevated temperatures. Although Zr and Hf have very similar properties, the fourth ionization potential of Zr (*c.* 34 V) is slightly but distinctly greater than that of Hf (*c.* 31 V). Also, although the radius of $Pb^{4+}$ is apparently a little greater than that of $Hf^{4+}$, $PbO_2$ has the rutile structure, and this could perhaps be caused in part by the fact that the fourth ionization potential of Pb (39·0 V) is distinctly elevated.

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## THE FLUORIDES OF K, Rb, Tl, AND $NH_4$

Discussion so far has dealt primarily with the possible significance of the effective field of a cation for determining structure, and the polarizability of the anion has been regarded as an important property. In this section some evidence of structural change which seems to be correlateable with deformability of the *cation* will be discussed. We recall the general rule that cations are most easily polarized in the field of the anion when they are large and univalent. Maximum cation deformation is apparently caused by $F^-$ (FAJANS; several papers). Consider now the fluorides of $K^+$, $Rb^+$, $Tl^+$, and $NH_4^+$ ($r$ varies from 1·33 to 1·44 Å); cation polarizability probably increases in the order, $K^+$, $Rb^+$, $Tl^+$, and $NH_4^+$. The structures of KF and RbF are ionic (NaCl), with little apparent distortion; co-ordination in TlF is still octahedral, but there is severe distortion, and instead of six equidistant F neighbours about Tl, the distribution is 2 (2·59 Å), 2 (2·75 Å), and 2 (3·04 Å). Such distribution is very similar to that in the one HgS dimorph—see above.) $NH_4F$ has the wurtzite structure with 4 : 4 co-ordination.* Structural changes in the sequence RbF—TlF—$NH_4F$ may be compared with those in the halides of mercury, thus:

| Octahedral | Distorted octahedral (2 : 2 : 2) | Tetrahedral |
|---|---|---|
| RbF<br>$HgF_2$ | TlF<br>$HgCl_2$<br>(HgS cinnabar) | $NH_4F$<br>$HgI_2$<br>(HgS metacinnabar) |

In each sequence, similar developments take place, but in the one, variable deformation of the cation may have been the cause, and in the other, variable polarization of the anion.

*Some general observations*

The data considered above provide quite distinct evidence of the existence of ionization potential threshold values which may serve to divide ionic from nonionic structures. Within the nonionic structure range there is evidence also of variation of structure with ionization potential. A question arising from this observation is whether extreme anion polarization deformation, involving perhaps serious rearrangement of electron distribution, might itself in part determine or at least influence bond disposition in nonionic inorganic compounds. It is one thing to draw attention to the existence of certain regularities and discontinuities, but another to develop a satisfactory theory to account for them. Such an attempt will not be made here, but attention will be drawn to some structures which have been explained on the basis of extreme anion polarization and not resonance hybridization. Such a hypothesis might ultimately serve as a useful model for basing a more general theory.

The structures of NaOH, KOH, RbOH, and CsOH are ionic (NaCl), whereas the

* This is usually attributed to hydrogen bonding.

dihydroxides of the alkaline earths and Cd, Mn, Co, Ni, and Zn (one dimorph only) are not ionic (fluorite or rutile, according to the size of the cation) but have the $CdI_2$ structure (compare with chlorides and bromides of the divalent metals). The hydroxides of the trivalent metals (Fe, Al, Cr?) with fairly small cations, contain hydroxyl bonds. BERNAL and MEGAW[9] have suggested that the ion $OH^-$ undergoes varying degrees of polarization, depending upon the field of the cation; polarization may be extreme, producing a separation of charges arranged tetrahedrally, and ultimately migration of H from one O to another. Change of structure and departure from simple ionic structures is suggested to arise from varying $OH^-$ ion polarization and hence not from some form of resonance hybridization. It might be possible to adopt such a scheme for various nonionic structures. Each anion will respond to the field of the cation in a different way; we have sufficient evidence to indicate that some anions are more polarizable than others, but we are not informed about the ways in which different anions will respond as the field of the cation becomes greater.

[9] J. D. BERNAL and H. D. MEGAW *Proc. Roy. Soc.* **A151**, 384 (1935).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 281 to 284. Pergamon Press Ltd., London

# THE PREPARATION OF ORTHOGERMANATES BY SINTERING REACTIONS: SOME NEW GERMANATES OF THE TYPE $A_2GeO_4$

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**Abstract**—It has been found that orthogermanates of the type $A_2GeO_4$ can be synthesized by sintering germanium dioxide with the corresponding oxides or carbonates. The calcium, strontium, barium, and cadmium compounds are being reported for the first time. X-ray powder-diffraction data for these compounds are included.

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## INTRODUCTION

JOHNSON[1] in an review of the inorganic compounds of germanium lists four orthogermanates of the formula $A_2GeO_4$ where A = Mg, Zn, Be, or Pb. SCHÜTZ[2] prepared zinc and beryllium orthogermanates by heating the respective oxide components in a furnace. He studied the reaction products by X-ray powder-diffraction methods and established their rhombohedral symmetry. It appeared to be of interest to investigate the possible synthesis of further orthogermanates by the method adopted by SCHÜTZ.

Metagermanates of the formula $AGeO_3$ where A = Ca, Sr, Ba, or Pb, have been prepared by precipitation from solution by MÜLLER and GULEZIAN,[3] and it was therefore of added interest to determine whether the reaction effected by the sintering of the solid oxide components occurred according to the scheme

$$AO + GeO_2 \rightarrow AGeO_3\text{—metagermanate}$$

or

$$2AO + GeO_2 \rightarrow A_2GeO_4\text{—orthogermanate.}$$

TABLE 1

| Reactants | Temperature in °C | Time in Hours | Appearance of reaction product | Constitution of reaction product |
|---|---|---|---|---|
| $2ZnO + GeO_2$ | 960 | 6 | White loosely sintered mass, not yellow when hot | $Zn_2GeO_4$ |
| $2BeO + GeO_2$ | 1100 | 6 | White loosely sintered mass | $Be_2GeO_4$ |
| $2MgO + GeO_2$ | 1100 | 6 | White loose powder | $Mg_2GeO_4$ |
| $2CaCO_3 + GeO_2$ | 1100 | 5 | White loose powder | $Ca_2GeO_4$ |
| $2SrCO_3 + GeO_2$ | 1050 | 6 | White sintered mass | $Sr_2GeO_4$ |
| $2BaCO_3 + GeO_2$ | 1060 | 6 | White loose powder | $Ba_2GeO_4$ |
| $2CdCO_3 + GeO_2$ | 1060 | 6 | White sintered mass | $Cd_2GeO_4$ |

[1] JOHNSON OTTO H. *Chem. Rev.* **51**, 457 (1952).
[2] SCHÜTZ W. *Z. physik. Chem.* **31B**, 292 (1936).
[3] MÜLLER J. H. and GULEZIAN C. F. *J. Amer. Chem. Soc.* **51**, 2029 (1929).

TABLE 2.—X-RAY POWDER-DIFFRACTION DATA

| $Ca_2GeO_4$ | | $Sr_2GeO_4$ | | $Ba_2GeO_4$ | |
|---|---|---|---|---|---|
| $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) |
| 4 | 5·54 | 2 | 3·63 | 6 | 3·46 |
| 3 | 4·74 | 4 | 3·36 | 2 | 3·15 |
| 8 | 4·33 | 2 | 3·24 | 9 | 3·04 |
| 2 | 4·10 | 4 | 3·08 | 10 | 2·98 |
| 1 | 3·84 | 10 | 2·92 | 3 | 2·71 |
| 4 | 3·35 | 1 | 2·62 | 4 | 2·54 |
| 4 | 3·30 | 5 | 2·45 | 5 | 2·44 |
| 6 | 3·06 | 4 | 2·34 | 5 | 2·26 |
| 6 | 2·96 | 5 | 2·18 | 5 | 2·13 |
| 10 | 2·78 | 2 | 2·10 | 3 | 1·993 |
| 2 | 2·61 | 5 | 2·08 | 2 | 1·939 |
| 2 | 2·53 | 1 | 1·922 | 2 | 1·926 |
| 5 | 2·38 | 5 | 1·884 | 2 | 1·800 |
| 4 | 2·18 | 2 | 1·834 | 1 | 1·775 |
| 3 | 2·08 | 2 | 1·727 | 7 | 1·728 |
| 3 | 2·04 | 7 | 1·701 | 6 | 1·661 |
| 5 | 1·935 | 4 | 1·667 | 3 | 1·490 |
| 6 | 1·819 | 3 | 1·588 | 5 | 1·451 |
| 3 | 1·764 | 3 | 1·567 | 4 | 1·394 |
| 2 | 1·730 | 4 | 1·467 | 4 | 1·339 |
| 7 | 1·691 | 1 | 1·453 | 2 | 1·305 |
| 7 | 1·657 | 4 diffuse | 1·395 | 2 | 1·277 |
| 4 | 1·491 | 3 | 1·347 | 5 | 1·195 |
| 4 | 1·450 | 4 | 1·253 | 3 | 1·178 |
| 1 | 1·362 | 4 | 1·225 | 3 | 1·163 |
| 3 | 1·316 | 3 | 1·202 | 3 | 1·133 |
| 3 | 1·308 | 2 | 1·172 | 6 | 1·044 |
| 4 | 1·240 | 5 | 1·154 | 3 | 0·998 |
| 1 | 1·213 | 3 | 1·135 | 2 | 0·949 |
| 3 | 1·188 | 5 | 1·113 | 6 | 0·936 |
| 4 | 1·155 | 2 | 1·057 | 5 | 0·914 |
| 2 | 1·101 | 5 | 1·047 | 2 | 0·873 |
| 2 | 1·074 | 2 | 1·012 | 3 | 0·875 |
| 3 | 0·981 | 2 | 0·996 | $4\alpha_1$ | 0·824 |
| 4 | 0·972 | 2 | 0·952 | $6\alpha_1$ | 0·808 |
| 3 | 0·946 | 2 | 0·945 | $7\alpha_1$ | 0·794 |
| 3 | 0·925 | 3 | 0·932 | $5\alpha_1$ | 0·783 |
| 1 | 0·916 | 3 | 0·915 | | |
| 2 | 0·888 | 5 | 0·898 | | |
| 2 | 0·857 | 4 | 0·875 | | |
| 2 | 0·828 | 2 | 0·866 | | |
| $3\alpha_1$ | 0·812 | $3\alpha_1$ | 0·809 | | |
| $4\alpha_1$ | 0·807 | $3\alpha_1$ | 0·796 | | |
| $3\alpha_1$ | 0·801 | $4\alpha_1$ | 0·784 | | |
| $2\alpha_1$ | 0·792 | | | | |
| $2\alpha_1$ | 0·784 | | | | |
| $3\alpha_1$ | 0·780 | | | | |

TABLE 2—(*continued*)

| $Cd_2GeO_4$ | | $Mg_2GeO_4$ | |
|---|---|---|---|
| $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) |
| 1 | 6·28 | 5 | 5·21 |
| 1 | 5·47 | 6 | 4·49 |
| 1 | 4·70 | 8 | 3·98 |
| 2 | 4·21 | 4 | 3·58 |
| 6 | 3·82 | 4 | 3·40 |
| 4 | 3·24 | 5 | 3·25 |
| 9 | 3·01 | 7 | 3·03 |
| 5 | 2·82 | 7 | 2·83 |
| 9 | 2·73 | 10 | 2·58 |
| 10 | 2·68 | 10 | 2·49 |
| 3 | 2·59 | 6 | 2·39 |
| 2 | 2·35 | 4 | 2·31 |
| 1 | 2·21 | 7 | 2·24 |
| 2 | 2·12 | 1 | 2·10 |
| 2 | 2·04 | 2 | 2·01 |
| 2 | 1·981 | 1 | 1·966 |
| 10 | 1·910 | 5 | 1·911 |
| 3 | 1·824 | 3 | 1·882 |
| 4 diffuse | 1·775 | 7 | 1·788 |
| 3 | 1·728 | 4 | 1·711 |
| 5 | 1·640 | 6 | 1·637 |
| 5 | 1·613 | 2 | 1·588 |
| 3 | 1·571 | 4 | 1·535 |
| 8 | 1·519 | 7 | 1·493 |
| 4 | 1·476 | 5 | 1·388 |
| 6 | 1·441 | 4 | 1·331 |
| 3 | 1·416 | 4 | 1·112 |
| 3 | 1·390 | 3 | 1·098 |
| 3 | 1·372 | 3 | 1·030 |
| 2 | 1·298 | 3 | 0·951 |
| 2 | 1·279 | 3 | 0·934 |
| 4 | 1·262 | 4 | 0·918 |
| 5 | 1·243 | 4 | 0·910 |
| 5 | 1·203 | 3 | 0·888 |
| 5 | 1·179 | 5 | 0·880 |
| 6 | 1·129 | $5\alpha_1$ | 0·867 |
| 6 | 1·116 | $6\alpha_1$ | 0·851 |
| 3 | 1·069 | $6\alpha_1$ | 0·846 |
| 3 | 1·022 | $5\alpha_1$ | 0·781 |
| 3 | 1·012 | $5\alpha_1$ | 0·775 |
| 6 | 0·993 | | |
| 5 | 0·964 | | |
| 4 diffuse | 0·956 | | |
| 2 | 0·943 | | |
| 3 | 0·922 | | |
| 5 | 0·907 | | |
| 3 | 0·896 | | |
| $3\alpha_1$ | 0·887 | | |
| $4\alpha_1$ | 0·869 | | |
| $5\alpha_1$ | 0·855 | | |
| $2\alpha_1$ | 0·839 | | |
| $2\alpha_1$ | 0·819 | | |
| $5\alpha_1$ | 0·810 | | |
| $4\alpha_1$ | 0·793 | | |
| $6\alpha_1$ | 0·783 | | |

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To investigate these reactions, intimate mixtures of the oxide or carbonate components were heated in an atmosphere of oxygen at temperatures between 900° and 1100° and for times varying between 2 and 12 hours and the reaction products studied by X-ray powder-diffraction methods.

## EXPERIMENTAL

Germanium dioxide, beryllium oxide, and cadmium carbonate supplied by British Drug Houses and analytical grade Merck's calcium, strontium, and barium carbonates and magnesium and zinc oxides were employed. The germanium dioxide was ignited at 1000°. Stoichiometric mixtures corresponding to the formation of the ortho and metagermanates were separately made by grinding in an agate mortar. The mixtures were heated in Morgan Triangle RR alumina boats in a Johnson-Matthey platinum-rhodium tube furnace with temperature control accurate to about ±5° C. An atmosphere of pure oxygen, dried by passing the gas successively through concentrated sulphuric acid and over potassium-hydroxide pellets, "Carbosorb", and "Anhydrone", was maintained in the furnace tube. At the end of an experiment, the specimen was removed rapidly from the furnace and allowed to cool in a desiccator.

X-ray diffraction photographs of the reactants and reaction products were obtained in a powder camera of 11·483-cm diameter with Straumanis mounting and using filtered copper $K\alpha$ radiation. Relative intensities were estimated visually. The X-ray wavelengths used were: Cu $K\alpha$ (mean)—1·5418 Å; Cu $K\alpha_1$—1·54051 Å.

## RESULTS AND DISCUSSION

The composition of the end-products was determined by the constancy of mass before and after reaction in the case of the oxide-oxide mixtures and by a loss of mass agreeing to within 2% of the theoretical evolution of carbon dioxide in the case of the carbonate-oxide mixtures. The X-ray diffraction photography showed in all instances that the reaction representing the formation of the orthogermanate

$$2AO + GeO_2 \rightarrow A_2GeO_4$$

was complete while the mixtures containing equimolecular proportions of the oxides showed the formation of the orthogermanate and an excess of germanium dioxide in the hexagonal ($\alpha$-quartz) form. This indicates the preferential formation of the orthogermanate to the metagermanate by sintering reactions between 900° and 1100°. The conditions most suitable for the synthesis of the orthogermanates are given in Table 1. The powder diffraction patterns of magnesium, calcium, strontium, barium and cadmium orthogermanates are given in Table 2; they are appreciably more complex than those of the corresponding zinc and beryllium compounds, indicative of the symmetry being lower than rhombohedral. It was in addition found that none of the orthogermanates investigated showed visible fluorescence under ultra-violet light.

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# COMPLEX FORMATION AND CATALYTIC ACTIVITY OF STANNIC AND PHOSPHORIC FLUORIDES*

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**Abstract**—Stannic and phosphoric fluorides are Friedel-Crafts catalysts. Both fluorides form compounds with aldehydes, ethers, nitriles, and amines. The criteria for catalytic activity are discussed.

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ALTHOUGH the catalytic activity of inorganic halides has been known since 1877, no reliable basis for predicting activity has yet emerged. In the acylation of toluene, probably the most extensively studied reaction for which catalysts have been arranged in order of reactivity,[1] the halides which are catalysts have the following properties in common: all have molecular, chain, or layer lattices, never three dimensional ionic lattices; all form complex halogen anions, stable in solid and solution, as well as complexes with organic molecules containing donor atoms (N, O, S). However, not all halides with the requisite lattices and co-ordinating ability are catalysts. (The division between active and inactive halides varies with the reaction, and to some extent is governed by experimental precision.)

The catalytic properties of stannic and phosphoric fluorides have been examined, bearing the criteria just mentioned in mind. The expectation that covalent phosphoric fluoride, which forms the stable $PF_6^-$ ion, would resemble boric fluoride has been verified. Phosphorus pentafluoride is an efficient catalyst. It polymerizes isobutene, at a rate comparable with that of boric fluoride,[2] and cyanogen chloride at a much slower rate. It forms solid compounds with ethers, both cyclic and linear, aldehydes, ketones, esters, nitriles, and amines. These have not been fully characterized, but all approximate to 1 : 1 compounds.

Stannic fluoride is regarded as an ionic fluoride (it sublimes at 705°) in contrast with the other molecular tetrahalides of Group IVa, and would not be expected to possess catalytic properties. It has been found that stannic fluoride forms complexes, such as $SnF_4 \cdot 2C_6H_5CHO$, $SnF_4 \cdot 2CH_3CN$, $SnF_4 \cdot 2C_3H_5N$, with organic compounds containing donor atoms, which are analogous to the six-covalent complexes of stannic chloride.[3] It also forms 1 : 1 adducts with cyclic, but not linear, ethers. It is soluble in alcohols, aliphatic fatty acids, esters, ketones, and amines. In some of the oxygenated solvents, part of the fluoride is replaced.

The catalytic ability of stannic fluoride in the acetylation of toluene is between that of the chloride and bromide. The optimum yield with stannic chloride is approximately 25% of ketone at 20–25°, with stannic fluoride 11%, and with stannic bromide less than 1%.[4] Stannic fluoride was unable to catalyse the polymerization of isobutene or cyanogen chloride.

* This work was carried out in 1953 during the tenure of a Turner and Newall Fellowship.
† Present address: A.E.I. Research Laboratory, Aldermaston, Berks.
[1] O. C. DERMER *et al. J. Amer. Chem. Soc.* **63**, 2881 (1941); **64**, 464 (1942).
[2] A. G. EVANS and G. W. MEADOWS *J. Polymer Sci.* **4**, 359 (1949).
[3] P. PFEIFFER *et al. Annalen* **376**, 285 (1910); **398**, 137 (1913).
[4] K. FIELD, M.Sc. thesis, Manchester (1953).

The structure of stannic fluoride is unknown, but the radius ratio $Sn^{4+}/F^-$ of 0·52, within the required limits for sixfold co-ordination, argues against a three dimensional ionic lattice, since ionic tetrahalides would require co-ordination numbers of 8 or more. A molecular lattice is even more improbable, becuse the density of molecular stannic iodide is less than that of stannic fluoride. HÜCKEL[5] has discussed this question at length and suggest a chain structure with octahedrally co-ordinated tin. Either this type of structure or a layer lattice seems probable.

It is concluded that the strong acceptor properties of stannic and phosphoric fluorides must be the factor which decides their similarity in chemical behaviour in spite of divergent physical properties. It seems that even a high lattice energy can be compensated by the strength of suitable co-ordination.

## EXPERIMENTAL

### *Preparation of stannic fluoride*[6]

Stannous chloride (Analar) was dehydrated by STEPHEN's method.[7] Bromine was added dropwise to 5-g portions of the anhydrous halide until the colourless liquid formed ($SnCl_2Br_2$) was distinctly brown, and the liquid was treated with 5–10 ml of bromine trifluoride. Most of the solvent was removed at 40° *in vacuo*, the remainder at 180°. To obtain quantitative conversions, care must be taken to avoid volatilization of the chlorobromide during addition of the trifluoride. (Found: e.w. 194·1. Sn 61·1, F 39·2, Br 0%. Calc. for $SnF_4$: equiv. weight 194·7, Sn 61·0, F 39·0%.)

The equivalent weights (e.w.) refer to the product of the molecular weight of the starting material and the weight ratio of product to starting material.

### *Reaction with organic compounds*

Organic liquids were dried and fractionally distilled by standard methods before use. Reactions were carried out by addition of liquid to fluoride and heating the mixtures. The excess, or unreacted, liquid was removed *in vacuo* until the residue was approximately of constant weight. The products were analysed by ROSE's method for fluorine, after decomposition with sodium carbonate solution. The tin was determined iodimetrically after reduction with aluminium and acid and a preliminary removal of organic matter by steam distillation. When the tin/fluorine ratio remained at 4, the products were water-soluble, but when loss of fluorine occurred the products rapidly gave precipitates in water. All the reactions in which compounds were formed were exothermic, and in order to avoid charring of organic material, both reactants were cooled before mixing.

*Benzaldehyde.* The solid formed after addition was broken up and heated to a homogeneous melt to complete the reaction. Some charring occurred. Excess of aldehyde was removed at 50° *in vacuo*. Found: e.w. 395, Sn 30·3, F 17·7%. $SnF_4$, $2C_6H_5CHO$ requires: e.w. 407, Sn 29·2, F 18·7%.

*Acetonitrile.* A bulky white solid, sparingly soluble in excess acetonitrile, formed. Found: e.w. 280, Sn 42·0, F 27·2%. $SnF_4 \cdot 2CH_3CN$ requires e.w. 277, Sn 42·9, F 27·4%.

*Pyridine.* The products obtained were slightly less than 1 : 2 compounds. A typical analysis is given. Found: e.w. 343, Sn 34·4, F 21·9, C 31·9, H 7·5, N 3·1%. $SnF_4$ 1·88 $C_5H_5N$ requires e.w. 343, Sn 34·6, F 22·1, C 32·8, H 7·7, N 2·8%. $SnF_4 2C_5H_5N$ requires e.w. 353.

*Trimethylamine.* These products were water soluble. Found: e.w. 265, F 28·6%. Calc. for $SnF_4$: 1·19 $N(CH_3)_3$: e.w. 265, F 28·8%.

1 : 4 *dioxane.* Found: e.w. 283, Sn 42·0, F 26·9%. $SnF_4 \cdot C_4H_4O_2$ requires e.w. 277, Sn 44·4, F 26·7%.

*Tetrahydrofuran.* Found: e.w. 264, Sn 45·5, F 29·5%. $SnF_4 \cdot C_4H_4O$ requires e.w. 267, Sn 44·5, F 28·5%.

*Diethyl and di-isopropyl ethers.* Stannic fluoride was insoluble in both ethers and could be recovered unchanged.

[5] W. HÜCKEL *Structural Chemistry of Inorganic Compounds* Elsevier Co. London Vol. II p. 474 (1951).
[6] A. A. WOOLF and H. J. EMELÉUS. *J. Chem. Soc.* 2865 (1949).
[7] STEPHEN *J. Chem. Soc.* 2786 (1930).

*Acetic acid* Stannic fluoride dissolved in acetic acid on heating. The solvent was removed at 60° *in vacuo* to leave a dry white solid which gave an immediate precipitate in water. Found: e.w. 250, Sn 44·6, F 14·0%. Calc. for $CH_3COOH{\cdot}SnF_4$: e.w. 255, Sn 46·6, F 29·8%. Calc. for $CH_3COOH{\cdot}SnF_2(OH)_2$: e.w. 251, Sn 47·4, F 15·1%.

The product obtained by removal of solvent *in vacuo* for 4 hr at room temperature (e.w. 382) retained 85% of the fluorine originally present in the tetrafluoride. This residue was initially water-soluble, but a precipitate slowly formed. The exact nature of the product is obscure, but it could form by elimination of hydrogen fluoride from a hydrate of stannic fluoride initially formed by dehydration of acetic acid. The alternative formation of acetyl fluoride seems less probable.

*Ethylene glycol.* A clear solution formed when both reactants were cooled before mixing. The solution was heated at 60–80° *in vacuo* to obtain a solid. The e.w. after 3 hr was 256, after 5 hr 247. Again fluorine was displaced. Found: e.w. 247, F 15·6%. Calc. for $SnF_2(OH)_2\ 0{\cdot}90C_2H_4(OH)_2$: e.w. 253, F 15·4%.

*Methyl ethyl ketone.* A viscid liquid remained after removal of solvent for two hours *in vacuo* at 60°. Found: e.w. 249, Sn 47·6; F 30·5%. Calc. for $SnF_4\ 0{\cdot}75CH_3\ COC_2H_5$: e.w. 249, Sn 47·8, F 30·5%.

Stannic fluoride was soluble in methanol, propanol, cyclohexanone, *p*-methyl acetophenone, ethyl acetate, and ethylene diamine. These solutions became viscous on concentration *in vacuo* without deposition of solids.

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### *Catalytic properties. Acetylation of toluene*

Acetyl bromide (0·9 g) was added to stannic fluoride (1·5 g) in toluene (15 ml) ($SnF_4/CH_3COBr$ = 1·1). The mixture, which soon became green, was left for three days at 25°. The ketone formed was determined gravimetrically with BRADY's reagent. 11% of the acetyl bromide was converted to ketone.

### *Polymerization of isobutene*

Isobutene, dried by repeated vacuum fractionation through traps at −80°, was passed into hexane which contained stannic fluoride and acetic acid (1 : 1). Methanol was added to the mixture after one day. No polymer precipitate appeared.

176-mm pressure of isobutene (1-litre bulb) was exposed to 1·6 g stannic fluoride which had been dissolved in acetic acid and evaporated to 2·8 g. *in vacuo*. The pressure decreased by 10 mm in 24 hr. This may have been caused by solution of isobutene in acetic acid and cannot be taken as evidence of polymerization.

### *Polymerization of cyanogen chloride*

Stannic fluoride (0·5 g) and cyanogen chloride (10 ml) were left in a sealed tube for 10 days. The liquid cyanogen chloride was removed *in vacuo*. The residual fluoride contained 2% chlorine, which is probably the residue from an addition compound and not cyanuric chloride. The reaction with nitrosyl chloride shows that such compounds exist.

### *Reaction with nitrosyl chloride*

The fluoride was left in contact with excess liquid nitrosyl chloride overnight. The excess chloride was removed *in vacuo* (0·01 mm). Found: e.w. 303, Cl 19·3%. Calc. for $SnF_4{\cdot}1{\cdot}65NOCl$: e.w. 303, Cl 19·35%.

In another experiment, in which excess nitrosyl chloride was removed at 10 cm pressure, the product contained more than two molecules of chloride to one of fluoride. Hence it seems probable that a compound $SnF_4{\cdot}2NOCl$ exists. Found: e.w. 338, F 21·7, N 8·0, Cl 23·5%. Calc. for $SnF\ 2{\cdot}18NOCl$: e.w. 338, F 22·5, N 9·0, Cl 22·9%.

*Phosphorus pentafluoride* was prepared from the pentachloride with arsenic trifluoride, fractionated and stored in a glass bulb. Reactions were performed by condensing an excess of pentafluoride on to weighed amounts of organic substances. The reaction vessel was allowed to warm and the reaction followed manometrically. A quantity of phosphorus pentafluoride was taken so that the final pressure in the system would not be less than 50 cm. When the reaction ceased the excess gas was condensed at −196° from the system within 30–60 seconds, and the residue weighed. This procedure resulted in partial volatilization of the compounds under the reduced pressure. With the higher boiling point organic substances the loss was not greater than 5%, but with the more volatile compounds it reached 15%. The reactions were exothermic, as with stannic fluoride.

The following solid compounds, judged by the approximate weight increases, were obtained: $C_6H_5CHO{\cdot}PF_5$; $CH_3CN{\cdot}PF_5$; dioxane $PF_5$; $CH_3COC_2H_5{\cdot}PF_5$, $CH_3COOC_2H_5PF_5$-$[(CH_3)_2CH]_2O{\cdot}PF_5$; $C_5H_5N{\cdot}PF_5$. Cyclohexanone formed a liquid product.

### *Polymerization of isobutene*

Phosphorus pentafluoride mixed with isobutene in the gas phase caused an immediate formation of solid and liquid polymer. A reaction followed manometrically (160 mm $PF_5$, 334 mm isobutene) was complete in less than two hours (final pressure, 158 mm).

### *Polymerization of cyanogen chloride*

Cyanogen chloride and phosphorus pentafluoride formed a clear solution, which solidified after a few days at room temperature.

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 289 to 295. Pergamon Press Ltd., London

# SEPARATION OF PROTACTINIUM FROM URANIUM RESIDUES

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**Abstract**—The chemistry of protactinium has recently become of interest in nuclear reactor technology. Weighable quantities of protactinium-231 were needed for investigations of its chemistry. A survey showed that one of the best sources of protactinium was a residue obtained in the processing of uranium minerals. This residue, which exists in tonnage quantities, contains a protactinium concentration of 0·1 to 0·3 part per million as determined by gamma-spectrum analysis. A relatively inexpensive method is described for the recovery of more than 90% of the protactinium in a high degree of purity.

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THE chemistry of protactinium has recently become of interest in nuclear reactor technology. One of its isotopes ($Pa^{233}$) is an intermediate in the thorium breeder cycle, being the parent of the fissionable isotope $U^{233}$.

In the past, pure protactinium has not been available in sufficient quantities for exhaustive chemical study. Today, the 233 isotope is produced synthetically, but its use in macro quantity for chemical study is limited by its rather high specific activity. The long-lived 231 isotope, which occurs naturally in uranium minerals, is more suitable for this purpose.

Only small quantities of $Pa^{231}$ have been isolated from various uranium residues.[1–5] It has been estimated that the total world production of this isotope is approximately 2 g.[4] In each case either the yield was low, or the purity questionable, or the method complicated and costly.

In this paper a simple and relatively inexpensive method is described for the separation of protactinium in high yield and purity from uranium residues. The method has been applied satisfactorily to the isolation of macro quantities of protactinium from large quantities of residues.

## SOURCE OF PROTACTINIUM

Analyses of various residues for protactinium showed that one of the best sources is an aqueous waste stream of the Mallinckrodt process for the extraction of uranium from pitchblende concentrates. ELSON *et al.*[5] employed this as the raw material in

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‡ Mound Laboratory is operated by Monsanto Chemical Co. for the US Atomic Energy Commission under Contract No. AT-33-1-GEN-53.
[1] A. VON GROSSE *Nature* **120**, 621 (1927); *Ber.* **61B**, 223 (1928).
[2] G. GRAUE and H. KADING *Naturwiss.* **22**, 286 (1934); *Angew. Chem.* **47**, 650 (1934).
[3] A. VON GROSSE and M. AGRUSS *J. Amer. Chem. Soc.* **56**, 2200 (1934); *Ind. Eng. Chem.* **27**, 422 (1935).
[4] L. I. KATZIN, Q. VAN WINKLE, and J. SEDLET *J. Amer. Chem. Soc.* **72**, 4815 (1950).
[5] R. ELSON, G. W. MASON, D. F. PEPPARD, P. A. SELLARS, and M. H. STUDIER, *J. Amer. Chem. Soc.* **73**, 4974 (1951).

their process for recovery of $Pa^{231}$. At that time this aqueous waste stream was described as a concentrated nitrate solution of essentially all the acid-soluble gross components of the ore concentrate except uranium, containing between 25 and 50% of the protactinium originally present in the ore. These investigators isolated the protactinium from this source with an overall yield of only 5–35%. The low yield was attributed to the poor extractability of protactinium into tributyl phosphate in the initial step of their method. It is now believed that the low extractability resulted because protactinium existed as a radiocolloid[6] in the aqueous waste stream.

Modifications in the Mallinckrodt process now produce an aqueous waste stream which contains a precipitate. This precipitate carries nearly all the protactinium that was originally present in the waste stream.[7] This precipitate was used as the source material for protactinium in the work described in this paper. It exists in tonnage quantity and, thus, is capable of yielding gram amounts of protactinium.

Since the source material is a residue from the processing of a naturally occurring mineral, some variation in its chemical and physical composition is to be expected. The following are some of its general properties. It is a wet, pasty filter cake which varies in colour from a light tan to a medium brown. The filter cake is approximately 50% solids and has a density of 1·6. Spectrographic analyses show that it is composed of iron, aluminium, calcium, magnesium, cobalt, and copper, with minor amounts of phosphorus, sodium, lead, silicon, nickel, manganese, and barium. Samples analysed by gamma spectrometry[8] showed a variable protactinium content of a few tenths of a part per million.

## RECOMMENDED PROCEDURE

The separation method described in this paper consists of three major steps: dissolution of the source material in dilute hydrochloric acid, concentration of the protactinium by precipitation of an internal silicate carrier, and final isolation of the protactinium by anion exchange in strong hydrochloric-acid solutions.[9] A flow sheet of the method is shown in Fig. 1. The distribution of protactinium is shown in parentheses. A yield of greater than 90% is obtainable, the principal loss being in the original hydrochloric-acid-insoluble residue.

The following recommended procedure is based on an initial charge of 200 g. Depending on the concentration of the source material, this charge should yield 25–50 $\mu$g of protactinium.

Slurry 200 g of the source material in a litre of 1N hydrochloric acid for 15 min. Longer digestion may be necessary for larger samples. Let settle (4–8 hours) until the supernatant liquid is clear, and decant or siphon the liquid. Centrifuge and wash the insoluble residue with 1N hydrochloric acid. (If the washing is omitted, the protactinium loss is about 5%.)

Dissolve 200 g of sodium chloride in the combined supernatant and wash liquids. Boil for 15 min to coagulate the silicate carrier. Let settle until the supernatant liquid is clear (about 4 hours), and carefully siphon off the liquid. (With care, the protactinium loss is less than 1%.) Centrifuge the silicate carrier and wash with water.

[6] G. K. SCHWEITZER and M. JACKSON *Radiocolloids*, U.S. Atomic Energy Commission, ORO-48.
[7] G. HARBOTTLE, in unpublished research, confirmed the observation that the filtered aqueous waste stream contained a negligible amount of protactinium.
[8] M. L. SALUTSKY, M. L. CURTIS, K. SHAVER, A. ELMLINGER, and R. A. MILLER *Analyt. Chem.* submitted.
[9] K. A. KRAUS and G. E. MOORE *J. Amer. Chem. Soc.* **72**, 4293 (1950), *ibid.* **77**, 1383 (1955).

Mix the silicate carrier with about 200 ml of 30% sodium-hydroxide solution, add 1 g of sodium carbonate, and boil to solubilize the silica and coagulate a basic precipitate (carbonates and hydroxides of iron, calcium, and cobalt). Centrifuge the precipitate, and wash three times with water. (Additional ferric hydroxide may precipitate from the caustic solution upon standing; however, it contains no appreciable quantity of protactinium.)

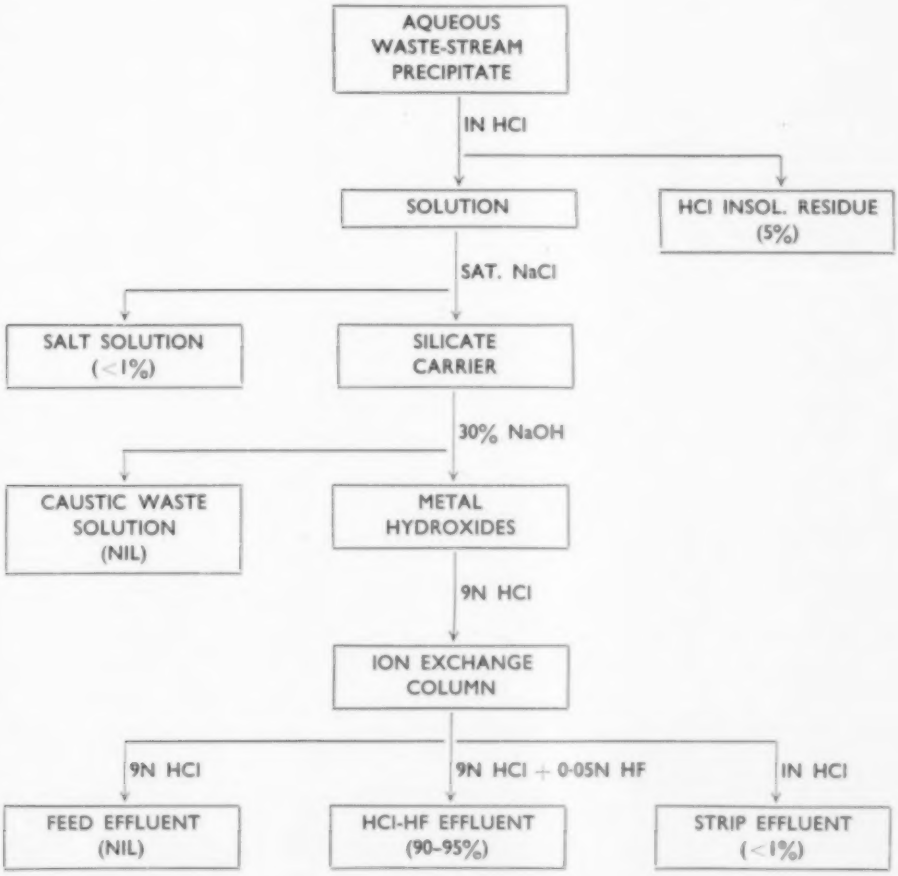


FIG. 1.—Flowsheet of the protactinium separation process.

Dissolve the precipitate in 25–50 ml of 9N hydrochloric acid. If a slight residue remains, centrifuge and discard the residue, since it has been shown to contain a negligible amount (<1%) of the protactinium.

Use the 9N hydrochloric-acid solution as the feed for the ion exchange column at a flow rate of 0·2 ml per minute per square centimetre. The resin should be pretreated with 9N hydrochloric acid. A suitable column has a resin bed of 100–200 mesh, 10% DVB, Dowex-1 resin of 2·2 cm diameter and 5·5 cm long. In this case, a column volume (i.e. volume of the bed) is approximately 20 ml.

Wash the column with several column volumes (3–5) of 9N hydrochloric acid. Elute the protactinium with 5-column volumes of 9N hydrochloric, 0·05N hydrofluoric-acid solution. Finally, strip the column of residual metals (mostly iron) with 1N hydrochloric acid.

Recover the protactinium from the hydrofluoric-acid solution by evaporation in a platinum container. A small amount of silicon picked up from the glass column may be eliminated by additional treatment with hydrofluoric acid.

## NOTES ON PROCEDURE

The source material was found to be more soluble in dilute hydrochloric acid than in any of the other common mineral acids. A maximum solubility of 90–95% of

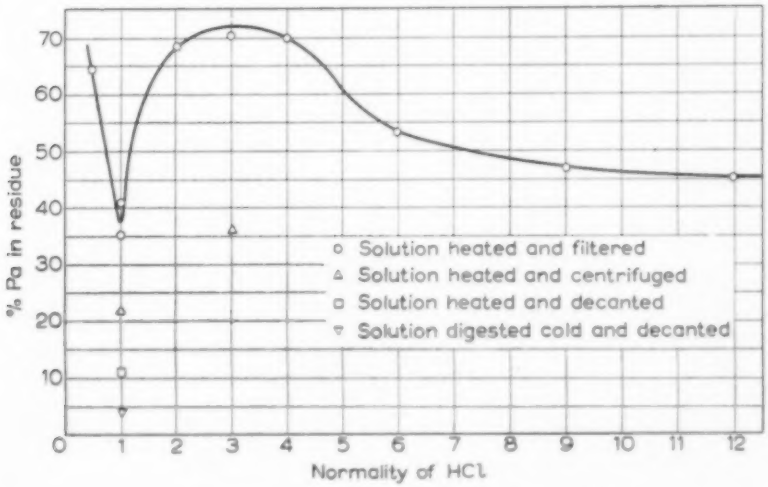


FIG. 2.—Effect of HCl concentration on Pa solubility

the total solids was obtained in 1N hydrochloric acid. Use of a stronger acid did not increase the solubility of the source material.

The greatest solubility of the protactinium was also observed in 1N hydrochloric acid. Fig. 2 shows the percentages of protactinium remaining undissolved in the insoluble residue when 10-g samples of the source material were digested with 50 ml of various hydrochloric-acid solutions. A minimum is obtained at 1N hydrochloric acid. For solutions less than 1N, a smaller fraction of the source material dissolves; hence, a greater percentage of the protactinium remains in the insoluble residue. For concentrations between 1N and 3N an increasing amount of protactinium remains in the residue. It seems that the higher acidities help coagulate a colloidal siliceous material which postprecipitates on the insoluble residue and carries the protactinium. Above concentrations of 3N hydrochloric acid, protactinium tends to form an anion chloride complex,[9] and its solubility increases. The two opposing effects cause a maximum at about 3N hydrochloric acid.

It is probable that the protactinium exists as a radiocolloid[6, 10] in the dilute

[10] A. G. MADDOCK and G. L. MILES *J. Chem. Soc.* 5248 (1948).

hydrochloric-acid solution. When the source material was heated with 1N hydrochloric acid and filtered on a fine-texture filter paper, 30–40% of the protactinium remained with the residue. Using the same treatment and centrifuging, the loss was reduced to 22%. If the residue was allowed to settle and the solution was decanted, the loss was only 11% When the source material was digested at room temperature and the solution decanted, only 4% was lost in the residue. Since heating helps coagulate a colloid, it would be disadvantageous to heat during the dissolution of the source material.

The weight of the silicate carrier was less than half a per cent of the weight of the original sample. The carrier from 20 g of the source material weighed only 57 mg. This resulted in a 400-fold concentration of protactinium. Spectrographic analysis indicated that it was composed of silicon, calcium, iron, magnesium, and traces of copper, cobalt, nickel, manganese, and aluminium. The material was amorphous, and an X-ray diffraction pattern was unattainable.

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The 30% sodium-hydroxide solution used to solubilize the silicate carrier was separated immediately from the basic precipitate. Less than 0·5% of the protactinium was in this caustic supernate. However, when the basic precipitate was permitted to remain in contact overnight (16 hours) with the 30% sodium-hydroxide solution, about 20% of the protactinium was found in the supernate. Such amphoteric properties have not previously been reported for protactinium.

Sodium carbonate was added to the caustic solution to aid in the coagulation of the basic precipitate. If fresh sodium hydroxide was used and no carbonate added, the hydroxide did not coagulate well, and some protactinium was lost in the suspension.

The feed effluent and wash from the ion-exchange column were evaporated to dryness, and the residue was analysed. Arc spectrographic analysis showed that it was composed of calcium, magnesium, manganese, nickel, aluminium, silicon, and a trace of copper. Thorium isotopes were detected in the feed effluent by gamma spectrum analysis.

During the addition of the feed and subsequent washing with 9N HCl, two coloured bands are observed to form in the resin bed. Iron is retained at the top of the bed and appears as a yellow band. Cobalt forms a green band which slowly moves down the bed. Cobalt is eluted at a faster rate in 9N hydrochloric acid than the protactinium, whereas iron is more tightly absorbed on the resin. If the addition of 9N HCl wash was continued to the point where the cobalt was eluted from the column, some loss of protactinium was observed.

When silica was removed from protactinium by evaporation with hydrofluoric acid in a platinum crucible, multiple treatment of the crucible with hot concentrated hydrochloric acid was necessary for the complete removal of protactinium from the platinum.

## RESULTS AND CONCLUSIONS

The results of one experiment in which every fraction was analysed for protactinium by gamma spectrometry[8] are shown in Table 1. Since a 5-g sample of the source material was used, the amounts of reagents given in the recommended procedure were scaled down accordingly. The material balance for protactinium is slightly greater than 100%; however, the accuracy of the analytical method[8] is ±5%. The recovery of 99% in the HCl-HF effluent is probably high by a few per cent. The gamma activity recovered from the HCl-HF effluent corresponds to 1·55 μg of

protactinium. Since the original sample weighed 5·65 g, the concentration of recoverable protactinium was 0·27 part per million. This concentration is identical with that determined by gamma-spectrum analysis of the source material.[8] Therefore, a very high yield was obtained by the method described in the recommended procedure.

The activity remaining on the resin bed was assumed to be due to protactinium and was determined by gamma-counting the resin after the column was stripped with

TABLE 1.—CONCENTRATION OF PROTACTINIUM BY THE RECOMMENDED PROCEDURE

| Fraction | c.p.m. at 300 keV | | % Pa |
|---|---|---|---|
| | Impurities | Pa | |
| HCl insoluble residue | 82 | 90 | 4·4 |
| Salt solution | 375 | Nil | — |
| Caustic waste solution | Nil | Nil | — |
| Feed effluent | 106 | Nil | — |
| HCl-HF effluent | Nil | 2,020 | 99 |
| Strip effluent | Nil | 15 | 0·7 |
| Loss on resin | — | 6 | 0·3 |
| Loss on glassware | 1 | 14 | 0·7 |
| Total | 564 | 2,145 | 105 |
| Original (5·65 g) | 511 | 2,044 | |

(Standard: 2155 c.p.m./1·65 $\mu$g Pa)

dilute hydrochloric acid. The glassware was leached with dilute hydrofluoric acid to determine the loss on its walls.

The radioactive purity of the protactinium was determined by gamma-spectrum analysis, by alpha-range analysis, and by alpha-spectrum analysis. The gamma spectrum of the purified protactinium is shown in Fig. 3. The photo peaks at 27, 95, and 300 keV are characteristic of protactinium. The very slight peak at about 150 keV is due to Compton electrons.[11] The low ratio between the 95- and 300-keV counts ($< 1{\cdot}3$) is also indicative that the degree of radiochemical purity of protactinium is high, since the presence of thorium isotopes would contribute considerably to the 95-keV peak.

An alpha absorption curve of a sample of the purified protactinium was prepared by counting the sample through various thicknesses of aluminium absorber in a windowless absorption counter.[12] The absorption curve of monoenergetic alpha particles when plotted on linear graph-paper is a straight line whose intercepts are the absolute counting rate and the range of the particles. In the case of a mixture of different energies, as in the case of protactinium-231, the range obtained from the curve is a function of the separate energies and the proportion of each present. For protactinium-231, using the alpha spectrum reported by COTTON, BOUISSIERES,

[11] S. GLASSTONE *Sourcebook on Atomic Energy*, pp. 68, 168–9, D. Van Nostrand Co., Inc., New York (1950)

[12] M. L. CURTIS and J. W. HEYD *Absolute Alpha Counting I: Determination of Backscattering Factors and Ranges, US Atomic Energy Commission, MLM-834*, 10 April 1953.

and ROSENBLUM,[13] the range in aluminium expected was 5·57 mg/cm². Data from the purified protactinium sample gave a range of 5·48. Assuming some self-absorption, the calculated and actual ranges were within experimental errors. Any substantial amount of thorium-230 (4·7 MeV alpha) in the protactinium sample would have shortened the range considerably. A second purification of the protactinium on a small column (2-ml capacity) was made prior to the alpha-range measurement. Alpha particles are quite easily absorbed, and a thin sample free from extraneous materials was required. The protactinium obtained by this treatment was essentially weightless with respect to nonradioactive contaminants.

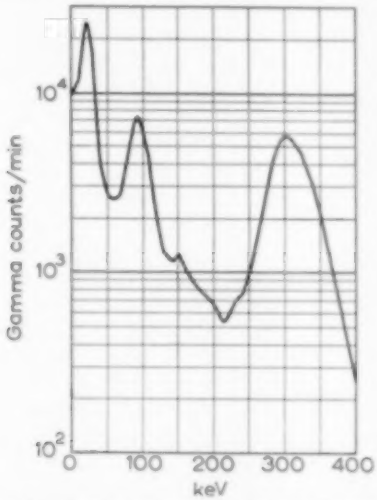


FIG. 3.—Gamma spectrum of purified protactinium-231.

For the alpha-spectrum analysis a sample of the protactinium, which had been purified by two ion-exchange steps, was mounted on a 1-in. platinum disc. The alpha spectrum was composed of one large peak and a small neighbouring peak. The particles producing the larger peak had a calculated 5-MeV energy, those of the smaller peak a slightly lower energy. This analysis indicates pure protactinium-231, which has an alpha spectrum essentially composed of 85% 5·0-MeV alpha particles and 15% 4·7-MeV alpha particles.[13]

In the separation of protactinium from uranium residues, a high yield, high radiochemical purity, and high chemical purity were obtained by the recommended procedure. Substitution of reagent-grade chemicals with industrial-grade chemicals (e.g. muriatic acid, tap water, rock salt, and soda ash) did not reduce the efficiency. When scaled up from 200 g to 11 lb of source material the procedure has worked efficiently, yielding ½ mg of protactinium. It has also been utilized in the inexpensive and efficient large-scale production of protactinium.

*Acknowledgement*—The authors would like to thank E. FAIRSTEIN and K. A. KRAUS of Oak Ridge National Laboratory for the alpha-spectrum analysis of the purified protactinium-231.

[13] E. COTTON, G. BOUISSIERES, and S. ROSENBLUM *Comptes rendus* **229,** 825 (1949); J. M. HOLLANDER I. PERLMAN, and G. T. SEABORG *Rev. Mod. Phys.* **25,** 469 (1953).

J. Inorg. Nucl. Chem., 1956, Vol. 3, pp. 296 to 299. Pergamon Press Ltd., London

# THE REACTION OF SULPHITE IONS IN SOLUTION WITH PERSULPHATE AND PYROSULPHATE

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**Abstract**—If dithionate is obtained by the reaction between persulphate and sulphite, one quarter of the dithionate sulphur comes from the persulphate and three quarters from the sulphite. An explanation is provided for this ratio.

If solid pyrosulphate is dissolved in an alkaline solution of sulphite some dithionate is formed. Each of the two reactants contributes half of the dithionate sulphur.

## INTRODUCTION

The usual way to prepare dithionate is by oxidation of sulphate with a solid oxide, e.g. $Fe(OH)_3$ or $MnO_2$, or by electrolytic oxidation. It is, however, mentioned in the literature[1] that oxidation of sulphite by means of persulphate can also produce dithionate, although the yield obtained is generally low. In this case analogy with the other preparation methods led us to expect that the dithionate sulphur would originate from the sulphite rather than from the persulphate, but we considered the matter of sufficient importance to investigate the problem by experimental means.

Accordingly we prepared radioactive sulphite and performed the oxidation with persulphate. From the reaction mixture the dithionate was isolated and the specific activity measued. Instead of being equal to that of the sulphite it amounted $\frac{3}{4}$ of this value (Table 1).

At this stage it was suggested that the reaction mechanism might be the following:

$$\left[\begin{matrix} & O & & & O & \\ O & S & O & O & S & O \\ & O & & & O & \end{matrix}\right]^{2-} + \left[\begin{matrix} & O & \\ O & S^{*} & \\ & O & \end{matrix}\right]^{2-} \rightarrow \left[\begin{matrix} & O & & O & \\ O & S & O & S^{*} & O \\ & O & & O & \end{matrix}\right]^{2-} + \left[\begin{matrix} & O & \\ O & S & O \\ & O & \end{matrix}\right]^{2-}$$

$$\left[\begin{matrix} & O & & O & \\ O & S & O & S^{*} & O \\ & O & & O & \end{matrix}\right]^{2-} = \left[\begin{matrix} & O & & O & \\ O & S^{\frac{1}{2}*} & O & S^{\frac{1}{2}*} & O \\ & O & & O & \end{matrix}\right]^{2-} \qquad (1)$$

$$\left[\begin{matrix} & O & & O & \\ O & S^{\frac{1}{2}*} & O & S^{\frac{1}{2}*} & O \\ & O & & O & \end{matrix}\right]^{2-} + \left[\begin{matrix} & O & \\ O & S^{*} & \\ & O & \end{matrix}\right]^{2-} \rightarrow \left[\begin{matrix} & O & O & & \\ O & S^{\frac{1}{2}*} & S^{*} & O & \\ & O & O & & \end{matrix}\right]^{2-} + \left[\begin{matrix} & O & \\ O & S^{\frac{1}{2}*} & O \\ & O & \end{matrix}\right]^{2-}$$

This assumption provided an attractive explanation of the specific activity of the dithionate. It was known that solid pyrosulphates can react with sulphite solutions to form dithionate,[2] but the assumption of the occurrence of pyrosulphate ions as an intermediate in aqueous solution was somewhat surprising.

[1] H. W. Albu and H. D. Graf von Schweinitz *Ber.* **65**, 729 (1932).
[2] P. Baumgarten *Ber.* **65**, 1645 (1932); *J. Chem. Soc.* 1569 (1936).

TABLE 1.—RADIOACTIVITY OF DITHIONATE FROM SULPHITE AND PERSULPHATE

| Oxidation of sulphite | Treatment of $BaSO_4$ | Ratio of specific activities of dithionate and of sulphite |
|---|---|---|
| By iodine | Not reprecipitated | 0·70 ± 0·02 |
| By iodine | Reprecipitated | 0·76 ± 0·01 |
| First by iodine, then bromine | Reprecipitated | 0·75 ± 0·03 |
| By bromine | Reprecipitated from picric acid solution | 0·71 ± 0·03 |

Each experiment represents an average of measurements on two or more samples, which were made to react, and were analysed separately. The deviations listed indicate the maximum difference from the average.

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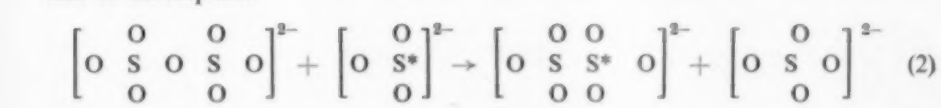
To test this possibility solid potassium pyrosulphate was dissolved in an alkaline solution of labelled sulphite. The liquid was worked up to give a dithionate fraction, which, if mechanism (1) were correct, should show a specific activity equal to $\frac{1}{2}$ of that of the sulphite.



(2)

Appreciable quantities of sulphur were obtained from the dithionate fraction and its specific activity was in good agreement with the value required by scheme (2) (Table 2).

TABLE 2.—RADIOACTIVITY OF DITHIONATE FROM SULPHITE AND PYROSULPHATE

| Oxidation of sulphite | Treatment of $BaSO_4$ | Ratio of specific activities of dithionate and of sulphite |
|---|---|---|
| By iodine | Not repreciptaited | 0·51 ± 0·03 |
| First by iodine, then bromine | Reprecipitated | 0·51 ± 0·01 |
| First by iodine, then bromine | Not reprecipitated | 0·50 ± 0·01 |
| First by iodine, then bromine | Reprecipitated | 0·50 ± 0·01 |
| By bromine | Reprecipitated from picric acid solution | 0·48 ± 0·01 |

Each experiment represents an average of measurements on two or more samples, which were made to react and analysed separately. The deviations listed indicate the maximum difference from the average.

These observations make it seem very likely that sulphite ions react with persulphate according to (1) and with pyrosulphate according to (2).

## EXPERIMENTAL

The radioactive sulphite solution was prepared by burning sulphur labelled with $S^{35}$ in a current of air and absorbing the dioxide in a sodium hydroxide solution.

For the reaction between sulphite and persulphate we used 1·15 moles of the former to 1 mole of

the latter in about 1 M NaOH. (In the literature the reaction is described in an acid medium, but then the yield of dithionate—indicated as equivalent to about 1% of the sulphite sulphur—is appreciably less than in our experiments, where it was around 3 or 4%.) The method used for the analysis of the reaction mixture was changed repeatedly in the course of the investigation. In the solution which had been acidified with hydrochloric acid, potassium iodide was used for the reduction of the excess persulphate and in the first runs iodine in sodium-iodide solution was added afterwards to oxidize a possible excess of sulphite. Barium chloride was added in excess, the barium sulphate formed was filtered off and the liquid containing the dithionate was mixed with a large quantity of nitric acid and evaporated to dryness. By this treatment the dithionate is hydrolysed to sulphate. The residue was dissolved in hydrochloric acid leaving the sulphur from the dithionate precipitated as barium sulphate. The specific activity of these samples was compared to that of barium sulphate obtained by oxidation and precipitation of the original sulphite solution (Table 1).

In later experiments the barium sulphate obtained in this way—which was considered to be of doubtful purity, as it might possibly be seriously contaminated by other inactive salts—was purified by boiling with an excess of sodium carbonate or potassium carbonate and reprecipitating with barium chloride from a hydrochloric acid solution. As we considered the possibility that the samples purified in this way might still contain some alkali salts, the standards were treated by the same reprecipitation procedure. In the last experiment the solution from which this precipitation was carried out contained 1% of a saturated picric-acid solution. This increases the purity of the precipitated barium sulphate,[3] and for this reason the standards were not subjected to a similar purification in this case.

Since polythionates—which were unlikely to be present anyway, but which we were anxious to exclude entirely as a possible contamination of our dithionate fraction—would not be oxidized by iodine, we added bromine (as $NaBrO_3 + NaBr$) after the iodine oxidation in some cases and instead of iodine in some others.

We also varied the time between different parts of the chemical treatment but this did not cause any difference in our results.

The reaction between radioactive sulphite and pyrosulphate was carried out in about 3 M sodium hydroxide. (The earlier descriptions of this reaction indicate an appreciably lower alkalinity.[2] However, under those circumstances the yield is much lower than by our method, where in many cases about $\frac{1}{4}$ mole of dithionate or even more can be obtained per mole of sulphite.) In the solution containing the labelled sulphite the solid potassium pyrosulphate was dissolved with very vigorous stirring. The ratio in which the two salts were mixed was varied by a factor 4 in one of the experiments and no influence on the result was noted. A satisfactory ratio is two molecules of $K_2S_2O_7$ per molecule of $Na_2SO_3$. Of course the larger part of the pyrosulphate does not react with the sulphite, but is hydrolysed very rapidly to sulphate. After the solid had dissolved the liquid was acidified with hydrochloric acid and the rest of the sulphite oxidized with iodine in sodium-iodide solution, iodine in sodium-iodide solution followed by bromine ($NaBrO_3 + NaBr$), or by bromine ($NaBrO_3 + NaBr$) alone and the sulphate precipitated by the addition of barium chloride. After filtration the liquid was evaporated to dryness with an excess of nitric acid, the residue dissolved in dilute hydrochloric acid and the dithionate sulphur separated as barium sulphate. The results are collected in Table 2.

In most cases the barium sulphate was purified as described under the sulphite-persulphate reaction, but in some cases this treatment was omitted.

Most of the samples that were counted were infinitely thick; in those cases where the thickness was less a correction was applied to take into account the self-absorption.[4]

## DISCUSSION

It remains to be discussed how reliable our figures are. According to BASSET and HENRY[5] nearly 1% of sulphite may be oxidized to dithionate by iodine in hydrochloric acid solution, and we ourselves have even obtained a somewhat higher figure.

[3] A. I. VOGEL *A Textbook of Quantitative Inorganic Analysis*, Longmans, Green and Co. London, second edition 1951, p. 498.
[4] A. H. W. ATEN, JR. *Nucleonics* **6**, No. 2, 68 (1950); *Natuurwetenschappelijk Tijdschrift* **32**, 155 (1950); *Chemisch Weekblad* **47**, 553 (1951).
[5] H. BASSET and A. J. HENRY *J. Chem. Soc.* 915 (1935).

As in all our experiments the excess sulphite is oxidized by iodine—possibly even in cases where only bromine is used as an oxidant since iodide is already present at this stage—small quantities of dithionate formed in this way with sulphur of specific activity equal to that of the original sulphite may contaminate the dithionate of our main reactions.

Using the most unfavourable figures we estimate that owing to this contamination the specific activity ratio of the sulphur from the dithionate and from the sulphite may be found too high by 0·04 in the case of the persulphate reaction and 0·02 in that of the pyrosulphate reaction. In many cases the error will be less.

Incomplete precipitation of the sulphate after the first oxidation would tend to make the dithionate activity too low, most seriously in the case of pyrosulphate reaction. Errors from this source seem to be very small, however.

The conclusion that contamination has not influenced our results more seriously than other sources of error, e.g. errors in the measurement of the radioactivity, is supported by the fact that the specific activity of the dithionate sulphur was not affected when the yield was varied by a factor 2 in the pyrosulphate reaction (due to differences in the quantity of pyrosulphate used) or when it varied by a factor 1·4 in the persulphate reaction (due to accidental differences in the circumstances of the reaction).

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# SOME ASPECTS OF THE FORMATION OF MOLYBDOPHOSPHATES IN AQUEOUS SOLUTION

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**Abstract**—The optimum acid concentrations, using perchloric acid, for the formation of 12-molybdophosphate in aqueous solutions have been determined. There are indications that the formation of a 6-molybdophosphate is a preliminary step in the formation of the 12-compound. In all solutions where the Mo/P ratio is less than 12, and in very dilute solutions at higher ratios also, there appear to be formed complexes with a Mo/P ratio less than 12.

It is also shown that change of temperature has a large and reversible effect on the optical absorption of the solutions.

## INTRODUCTION

THE factors affecting molybdophosphate formation in aqueous solutions are:

concentration of acid—effect of the hydrogen ion and/or the un-ionized acid,
phosphate concentration,
molybdate concentration,
temperature.

FERRARI[1] has claimed that time is also an important factor. In a study of the light absorption of molybdenum blue, obtained by reduction of the 12-molybdophosphate, he has shown that the optical density increases with the time of standing allowed prior to reduction. This leads him to postulate two forms of the acid, the one first formed being metastable and being slowly converted into the more stable form. Support for this postulate is to be found in the work of STRICKLAND[2] and FERRARI,[3] who have both observed this phenomenon for 12-molybdosilicic acid, and have proved it to exist as $\beta$ (metastable) and $\alpha$ (stable) forms. In the case of this acid a definite decrease in the yellow colour is discernible; since no such change has been reported for 12-molybdophosphoric acid FERRARI's proposal seems doubtful.

The majority of workers have recognized that the acid concentration must lie between definite limits for 12-molybdophosphate formation to be possible. JANDER and WITZMAN[4] observed that there was no change in the diffusion coefficient or in the absorption spectrum for a molybdate solution in the presence or absence of phosphate when the *p*H was greater than 2. BOLTZ, DE VRIES and MELLON[5] have shown that above *p*H 2·7 the polarographic wave for 12-molybdophosphate approaches that for molybdate.

[1] C. FERRARI *Gazzetta.* **81,** 795 (1951)
[2] J. D. H. STRICKLAND *J. Amer. Chem. Soc.* **74,** 862 (1952).
[3] C. FERRARI *Gazzetta.* **81,** 692 (1951).
[4] G. JANDER and H. WITZMAN *Z. anorg. Chem.* **215,** 310 (1933).
[5] D. V. BOLTZ, T. DE VRIES and M. G. MELLON *Analyt. Chem.* **21,** 563 (1949).

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On the basis of dialysis measurements, JANDER and DREWS[6] suggest that 12-molybdophosphoric acid decomposes in strongly acid solution with the formation of molybdenyl cations:

$$H_3PO_4(Mo_3O_9)_4 + 24HNO_3 \rightarrow H_3PO_4 + 12MoO_2(NO_3)_2 + 12H_2O.$$

JANDER further suggested that 12-molybdophosphate exists as such in concentrated solution but that in dilute solution it is hydrolysed to hexamolybdate and 6-molybdophosphate:

$$PO_4(Mo_3O_9)^{3-} + 6H_2O \rightleftharpoons H_3Mo_6O_{21}^{3-} + (H_2PO_4)(H_3Mo_6O_{21})^{4-} + 4H^+.$$

LINDQVIST[7] suggested that the transformation from $Mo_7O_{24}^{6-}$ to $Mo_8O_{26}^{4-}$ proceeds via a transient $Mo_6O_{22}^{8-}$ ion. It may similarly be argued that 12-heteropoly-acid formation involves a transient 6-molybdophosphate (-arsenate, etc.) ion. The major objection to a 6-molybdophosphate ion is the necessity to postulate an octahedral phosphorus atom. This occurs in $HPF_6$ and $KPCl_6$ but has not so far been found with oxygen as the donor atom. Since, however, oxygen in both covalent and ionic bonding is the same size as fluorine (while chlorine is considerably larger) the co-ordination [P—(O—Mo—)$_6$] is not inherently impossible.

SOUCHAY and FAUCHERRE[8] claim to have shown the existence of 11, $2\frac{1}{2}$, and 1 molybdophosphates, and of a 9-molybdophosphate in concentrated solutions, by cryoscopic and potentiometric methods. No satisfactory evidence for the first three ions has ever been put forward.

Colorimetric and spectrophotometric methods for the estimation of phosphate, based on the yellow colour of the 12-molybdophosphate complex, have been studied by a number of workers.[9–12] BOLTZ and MELLON[9] have shown that for 0·000147M phosphate the optical density increases with the molybdate concentration up to 0·0188M (i.e., Mo/P = 128); further increase in the molybdate concentration did not influence the optical density. Water was used as the blank; the increased absorption may, therefore, have been due to absorption by molybdate itself. The experimental data do not permit a final decision to be made on this point, because no wavelengths are quoted for this section of the work. Like VEITCH[10] and KRUMHOLZ,[13] BOLTZ and MELLON recognised a definite range of acid concentrations for the establishment of maximum optical density; for the phosphate and molybdate concentrations quoted, this range was 0·2–0·3N (nitric or hydrochloric acid) i.e. *p*H 0·5–0·8.

BABKO and SHANOVSKAYA,[14] using a colorimetric method, have shown that at room temperatures and higher acidities (*p*H 0·7–1·3) the maximum colour occurs when the ratio of Mo : P in the solution is 24 : 1, but at *p*H 2·0 the maximum colour occurs at a ratio of 12 : 1. At 60°C, however, the maximum colour at all *p*H values

[6] G. JANDER and E. DREWS *Z. physikal. Chem.* **190,** 217 (1942).
[7] I. LINDQVIST *Nova Act. Reg. Sci. Upsaliensis* (4) **15,** no. 1 (1950).
[8] P. SOUCHAY and J. FAUCHERRE *Bull. Soc. Chim.* (5) **18,** 355 (1951).
[9] D. F. BOLTZ and M. G. MELLON *Analyt. Chem.* **20,** 749 (1948).
[10] F. P. VEITCH *J. Amer. Chem. Soc.* **25,** 169 (1903).
[11] A. JOLLES and F. NEURATH *Monatsh.* **19,** 5 (1898).
[12] A. G. WOODMAN and L. L. CAVYAN *J. Amer. Chem. Soc.* **23,** 96 (1901).
[13] P. KRUMHOLZ *Z. anorg. Chem.* **212,** 91 (1933).
[14] A. K. BABKO and S. S. SHANOVSKAYA *J. Gen. Chem. (USSR)* **23,** 389 (1953).

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corresponds to the ratio 12 : 1. When they attempt a calculation of the instability constant of the complex they seem to assume a 12 complex at room temperature and *p*H 1·0!

The increase in colour with temperature has received frequent notice, for example FERRARI has mentioned that some solutions which are colourless at room temperature become yellow on warming.

Earlier work by two of the present authors[15, 16] has shown that, at a given wavelength, solutions of molybdate show maximum absorption at a particular acid concentration; further increase in the acid concentration caused a reduction in the

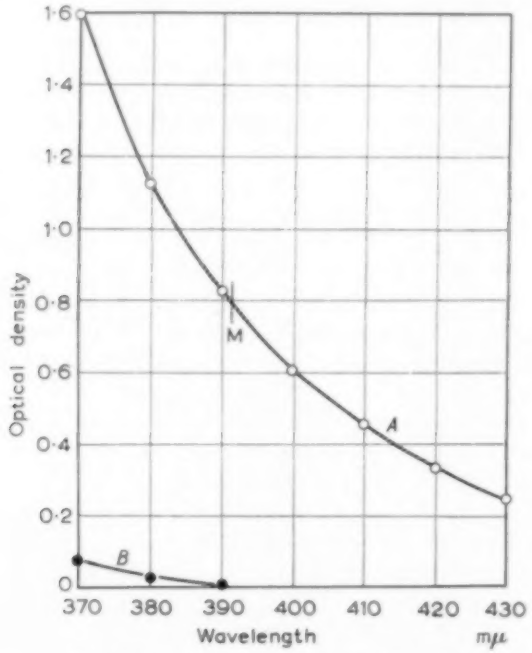


FIG. 1.—Graph of optical density against wavelength.
*A*—0·05M sodium molybdate, 0·3N perchloric acid, 0·002M sodium dihydrogen phosphate.
*B*—0·05M sodium molybdate, 0·3N perchloric acid, no phosphate.

optical density. The existence of a similar optimum acidity for solutions containing molybdate together with phosphate seems evident from the results of the other workers already mentioned, though no systematic quantitative investigation has been reported. It was with the need of such a study in mind that the present work was undertaken; the initial results and their implications are dealt with in this paper.

## EXPERIMENTAL

Originally no thermostat cell was available, but to minimize suspected temperature effects, readings were taken as far as possible at the same temperature. Moreover, the crucial results shown in Fig. 2, on which equation (1) is based, were all made within a short space of time on solutions that had been brought to thermal equilibrium, the ambient temperature remaining 19·6°C.

All extinction measurements were made in 10-mm and 2-mm fused silica cells on a Unicam SP 500 spectrophotometer.

Phosphate solutions were prepared from A.R. $NaH_2PO_4.2H_2O$.

Molybdate solutions were prepared from laboratory reagent grade $Na_2MoO_4.2H_2O$.

Perchloric acid was the only acid used, the objections against hydrochloric, nitric, and sulphuric acids having been mentioned previously.

Fuller details of the experimental methods are contained in earlier papers.[15, 16] The methods whereby optimum conditions were determined are apparent from ref. 16 Fig. 1.

After the work on concentration effects had already been completed, a thermostated cell-carrier for the spectrophotometer, made according to the directions of GRANT[17] was acquired. This made possible a preliminary study of the effect of temperature.

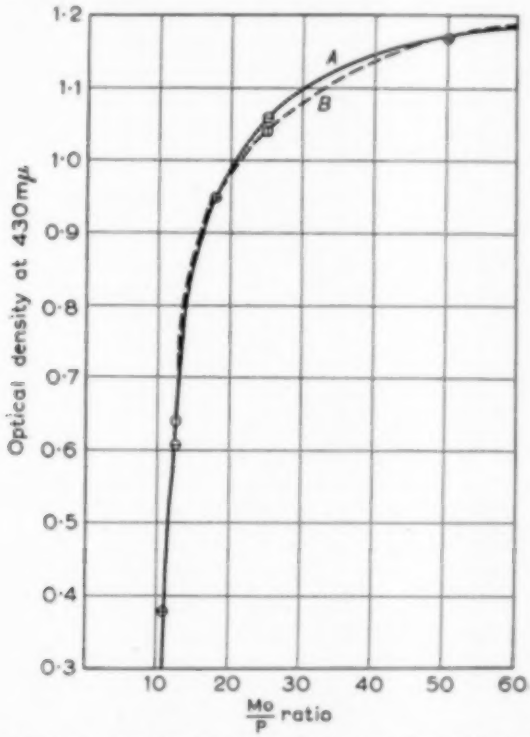


FIG. 2.—Graph of optical density against Mo/P ratio: for 0·002M phosphate at 430 mμ.
*A*—experimental curve.
*B*—calculated curve.

## RESULTS AND DISCUSSION

Fig. 1 shows the variation in the absorption spectrum of acidified molybdate solutions in the presence and absence of phosphate. By working above a certain minimum wavelength it is possible to obtain an optical density which is proportional to molybdophosphate only (wavelengths above point *M* in Fig. 1). Since the accuracy of the optical density measurements is 0·01 it is permissible to consider this minimum wavelength as that at which the equivalent solution, without phosphate, has an optical density of 0·01. Some wavelengths at which this is the case are given in Table 1.

[15] P. J. COOPE and W. P. THISTLETHWAITE *J. Inorg. Nucl. Chem.* **2**, 125 (1956).
[16] P. J. COOPE and W. P. THISTLETHWAITE *J. Inorg. Nucl. Chem.* **3**, 24 (1956).
[17] J. K. GRANT *Chem. and Ind.* 942 (1955).

For 0·0004M phosphate solutions the optical density measurements, at the threshhold wavelength, were too small to be considered reliable (i.e. less than 0·8). The same optimum conditions as those indicated at the threshold wavelength appear,

TABLE 1

| molybdate concentration | 0·1M | 0·05M | 0·025M | 0·01M | 0·005M |
|---|---|---|---|---|---|
| wavelength, 10-mm cell | 430 mμ | 420 mμ | 410 mμ | 390 mμ | 380 mμ |
| wavelength, 2-mm cell | 400 mμ | 390 mμ | 380 mμ | 370 mμ | 360 mμ |

however, to apply at shorter wavelengths (even though these involve higher optical densities which cannot be considered independent of absorption by isomolybdate). The optimum acid concentrations, for maximum optical density, for solutions

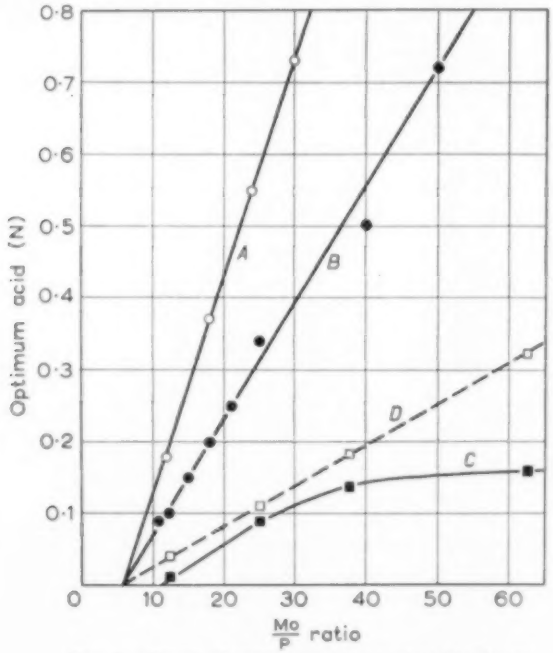


FIG. 3.—Graph of optimum acidity against Mo/P ratio.
*A*—0·005M sodium dihydrogen phosphate.
*B*—0·002M sodium dihydrogen phosphate.
*C*—0·0004M sodium dihydrogen phosphate (experimental).
*D*—0·0004M sodium dihydrogen phosphate (calculated).

0·0004M in phosphate and 0·025M, 0·015M, 0·01M and 0·005M in molybdate are shown on Fig. 3. In the case of 0·0004M phosphate and 0·005M molybdate the solution at the optimum acidity and for some way above is colourless; but at 0·05N acid the solution is coloured yellow. It appears, therefore, that the optimum acidity, determined with the spectrophotometer, refers to some complex, other than 12-molybdophosphate, having no visual colour.

For 0·002M phosphate and 0·1M, 0·08M, 0·05M, 0·042M, 0·036M, 0·03M, and 0·025M molybdate the optimum acidities, found from the optical densities at the minimum wavelengths permitted after consideration of Table 1, are shown on

Fig. 3. For solutions with the Mo/P ratio less than 12 the optical density rapidly approaches that for molybdate alone. In the case of Mo/P = 11 the optical density at 410 m$\mu$ and 0·09N acid (the probable optimum acidity) is 0·71; for Mo/P = 12·5 at 410 m$\mu$ and 0·10N acid the value is 1·38.

For 0·005M phosphate and 0·15M, 0·12M, 0·09M, and 0·06M molybdate the optimum acidities are given on Fig. 3. These optimum acidities are again calculated from the optical densities at the minimum wavelength permitted by Table 1.

For a discussion of the significance of the optimum acidity, the results obtained for phosphate concentration 0·002M (the middle of the three concentrations used) has been chosen. The effect of variation in the Mo/P ratio for this concentration of phosphate at the optimum acidities in each case is shown in Fig. 2. The optical densities were all measured in 10-mm cells at 430 m$\mu$ and 19·6°C (the corresponding molybdate solutions all have negligible absorption at 430 m$\mu$). The optical density may be assumed to be proportional to the concentration of the yellow molybdophosphate. The curve in the figure has the form of a rectangular hyperbola and is closely fitted by the empirical equation:—

$$E = \frac{12{\cdot}28 - 1{\cdot}24\text{Mo/P}}{(7{\cdot}4 - \text{Mo/P})} \qquad (1)$$

where $E$ = optical density at 430 m$\mu$ and 19·6°C in a 10-mm cell. The curve calculated from this equation is also shown on the figure and the experimental and calculated values of $E$ are compared in Table 2.

TABLE 2

| Mo/P | 11·0 | 12·5 | 18·0 | 25·0 | 50·0 |
|---|---|---|---|---|---|
| Experimental $E$ | 0·38 | 0·64 | 0·95 | 1·04 | 1·17 |
| Calculated $E$ | 0·38 | 0·61 | 0·95 | 1·06 | 1·17 |

No theoretical significance is apparent in equation (1) but it may be used to establish the maximum optical density of 1·24 corresponding to infinite Mo/P ratio, which is the point at which the phosphate exists entirely as the yellow molybdophosphate. All the molybdophosphates that have been precipitated from solutions in which the Mo/P ratio is greater than 12 have been shown, by analysis, to have a Mo/P ratio of 12. Similarly, all molybdophosphoric acids extracted with organic solvents from solutions in which the Mo/P ratio is greater than 12 have been shown to have a Mo/P ratio of 12. BABKO and SHANOVSKAYA have indicated the possibility of a molybdophosphate in solution with a Mo/P ratio of 24; such a complex seems unlikely from structural considerations, and the present results rule out that possibility. The reasons are as follows. If the colour were due to a 24-acid, the maximum optical density permitted by the available molybdate at the lower ratios would be as shown in Table 3.

TABLE 3

| Mo/P ratio in solution | 11 | 12·5 | 18 | 25 |
|---|---|---|---|---|
| Max. optical density (due to 24-acid) | 0·55 | 0·62 | 0·89 | 1·24 |
| Experimental optical density | 0·38 | 0·64 | 0·95 | 1·04 |
| Max. optical density (due to 12-acid) | 1·10 | 1·24 | 1·24 | 1·24 |

From the curve it is apparent that, whatever the size of the complex present, its complete formation does not occur even at solution ratios well above 24; assumption of a 24-acid implies, however (Table 3), that formation is complete at solution ratios that are less than 24. If a similar argument is applied, but a 12-acid assumed (last row of Table 3), the experimental values never approach the permissible; this is to be expected from the form of the curve. It may, therefore, be concluded that the complex here investigated is the 12-molybdophosphoric acid.

Fig. 3 shows that the graphs of optimum acidity vs. Mo/P ratio for 0·002M and 0·005M phosphate are straight lines passing through Mo/P = 6 for zero acid.

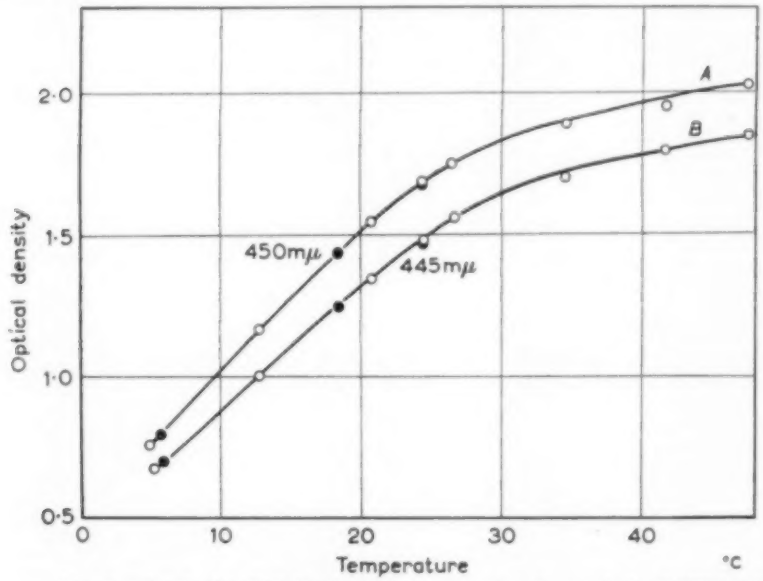


FIG. 4.—Graph of optical density against temperature for a solution 0·002M in P, 0·05M in Mo, 0·34N in $HClO_4$.
*A*—at 450 mμ.
*B*—at 445 mμ.

The complex being formed in these cases is regarded as the 12-molybdophosphoric acid (see above). The equations for both the straight lines may be written in the general form:

$$\text{optimum acid} = \text{Mo/P} - 6\text{P}^{0\cdot60}. \qquad (2)$$

For 0·0004M phosphate the line is not straight; this may indicate that absorption in this case is not *wholly* due to the 12-acid. The optimum acidities for 0·0004M phosphate, calculated from eq. (2), are:—

| Mo/P | 12·5 | 2·5 | 37·5 | 62·5 |
|---|---|---|---|---|
| Calculated optimum | 0·04 | 0·11 | 0·18 | 0·32 |
| Experimental Optimum | 0·01 | 0·09 | 0·14 | 0·16 |

The curve representing the calculated optima is also shown on Fig. 3.

The fact that the two straight lines, for 0·002M and 0·005M phosphate, pass through Mo/P = 6, at zero acidity, suggests that a molybdophosphate ion of this

ratio is formed in solutions of molybdate plus phosphate in the absence of acid. The addition of acid would then appear to be necessary for the formation of the larger complex by condensation between this 6-complex and isopolymolybdate ions. This idea is in line with JANDER's suggestion (6), about the hydrolysis of 12-molybdophosphate, and with LINDQVIST's suggestion of a transient hexaion in the iso-system.

After the described work was completed, a thermostated cell carrier became available. Some preliminary experiments on the effect of temperature on isomolybdate and molybdophosphate systems were undertaken. This work shows (a) that the absorption of the iso-system is virtually independent of temperature in the range 25–50°C for all wavelengths; (b) that absorption by the molybdophosphate system over a similar temperature range is remarkably temperature-dependent. For 0·002M phosphate the variation of absorption with temperature at 445 and 450 m$\mu$ is shown on Fig. 4. Readings were reproducible on cooling the heated solutions.

It is not possible to discuss this effect fully until further work has been done, and such work is not possible with the present equipment. It will merely be noted here that (a) the effect of temperature is reversible; (b) the magnitude of the effect indicates a reversible chemical change (ion aggregation) rather than a mere increase in the extinction coefficient of a single absorbing species.

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# THE ABSORPTION SPECTRA OF COMPLEX OXALATES

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(*Received* 11 *July* 1956)

**Abstract**—The ultra-violet absorption spectra of oxalic acid, its simple salts, and numerous complex metallic oxalates have been determined. For many complex oxalates the absorption spectra support structures in which the metal-oxalate bonds are covalent; some further support is provided by observations in the infra-red. A shift in wavelength of absorption of the co-ordinated oxalate group is related to the strength of the electric field in the neighbourhood of the co-ordinating metal cation.

THE absorption spectra of aqueous solutions of oxalic acid and potassium oxalate and of methyl oxalate in hexane were determined by LEY and ARENDS[1] and by SCHEIBE;[2] in the absorption of methyl oxalate a band of low intensity (extinction about 50) at a wavelength of about 250 m$\mu$ appeared as a marked shoulder on a band of high intensity, which extends into the far ultra-violet. This low-intensity band did not appear in the absorption of potassium oxalate, but was observed as an inflexion in the absorption curve of oxalic acid (Fig. 1). A similar low-intensity band appears in the absorption of many carboxylic acids and their esters, usually at slightly shorter wavelengths, but not in the absorption of their salts. The appearance of a band of low intensity in the region 210–260 m$\mu$ is thus characteristic of the covalently bound carboxyl group and probably represents transitions of the $\pi$-electrons of the carbonyl group, transitions which do not occur in the carboxylate ion owing to the equivalence of the oxygen atoms.

The different natures of carboxyl groups in acids, esters, and salts is also shown in the infra-red region, particularly in the C=O stretching fundamentals in the region 1600–1750 cm$^{-1}$. In esters this absorption usually occurs about 1720–1750 cm$^{-1}$ and in salts about 1600–1630 cm$^{-1}$.

Many carboxylic acids are capable of forming complex anions with metals, such complexes being particularly stable when chelation can occur, as with oxalic acid, and the absorption spectra of such complexes should give direct evidence of the nature of the metal-carboxylate linkage by distinguishing between carboxyl groups involved in ionic and covalent bonding. This distinction is of particular interest in view of the properties of the ferri-oxalate ion. Magnetic data place this ion in the category of complexes designated ionic by PAULING and now generally thought to contain metal-oxygen bonds which are covalent, but in which the 4*d* orbitals of the metal atom are used in hybridization, leaving unpaired electrons in the 3*d* orbital to account for the magnetic properties of the complex ion.

In a previous publication[3] certain complex oxalates were shown to have absorption spectra similar to that of methyl oxalate, thus supporting structures for

[1] H. LEY and B. ARENDS *Z. phys. Chem.* (B) **17**, 177 (1932).
[2] G. SCHEIBE *Ber.* **59**, 1321 (1926).
[3] D. P. GRADDON *Chem. and Ind.* 80 (1956).

the complex ions in which the metal-oxygen bonds are covalent. A wider range of complex oxalates has now been examined by ultra-violet and infra-red methods, with the following results.

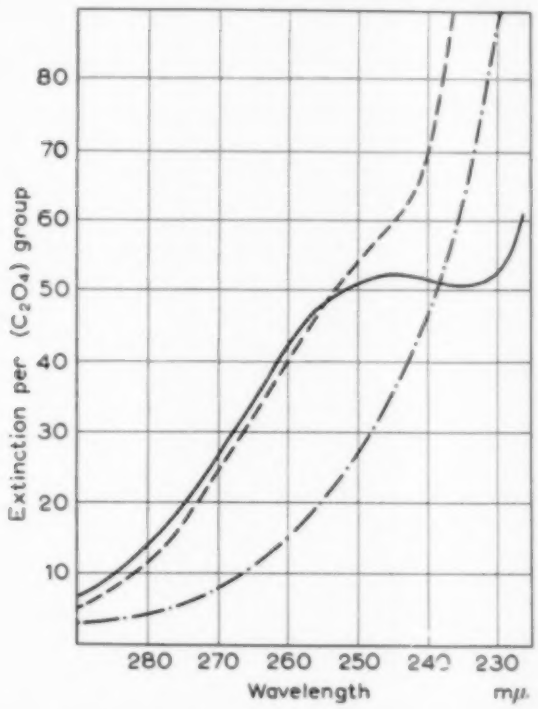


FIG. 1.—Absorption spectra of 0·01 M oxalic acid in water – – – – –;
0·01 M potassium oxalate in water — · — · —;
0·01 M methyl oxalate in methanol ————.

## 1. ULTRA-VIOLET SPECTRA

### 1.1. *Oxalic acid and its salts*

LEY and ARENDS' examination of oxalic acid was carried out in dilute aqueous solution in which oxalic acid is appreciably dissociated into ions. With acid dissociation constants of $5{\cdot}9 \times 10^{-2}$ and $6{\cdot}4 \times 10^{-5}$, 0·01 molar aqueous oxalic acid is 88% dissociated into $H^+$ and $(HC_2O_4)^-$ ions, secondary ionization being negligible. The absorption of light by oxalic acid at this concentration is thus mainly attributable to the $(HC_2O_4)^-$ ion. The ionization is suppressed in the presence of mineral acids, so that if 0·1 molar hydrochloric acid is used as solvent, only 37% of the oxalic acid is ionized and in 1·0 molar hydrochloric acid this is reduced to 6%, the absorption of the last solution being almost wholly attributable to nonionized oxalic acid molecules.

The absorption spectra of solutions of oxalic acid in dilute hydrochloric acid were found to approach that of methyl oxalate as the concentration of hydrochloric acid increased (Fig. 2), the hydrogen atoms in molecular oxalic acid being covalently

bound as indicated by the appearance of the characteristic low-intensity band about 250 m$\mu$. This band was also observed in the absorption of a solution of oxalic acid in 93% sulphuric acid, but displaced slightly to shorter wavelength, presumably due to solvent effect.

The absorption of the $(HC_2O_4)^-$ ion was determined in 0·01 molar aqueous potassium hydrogen oxalate in which dissociation and hydrolysis of the $(HC_2O_4)^-$

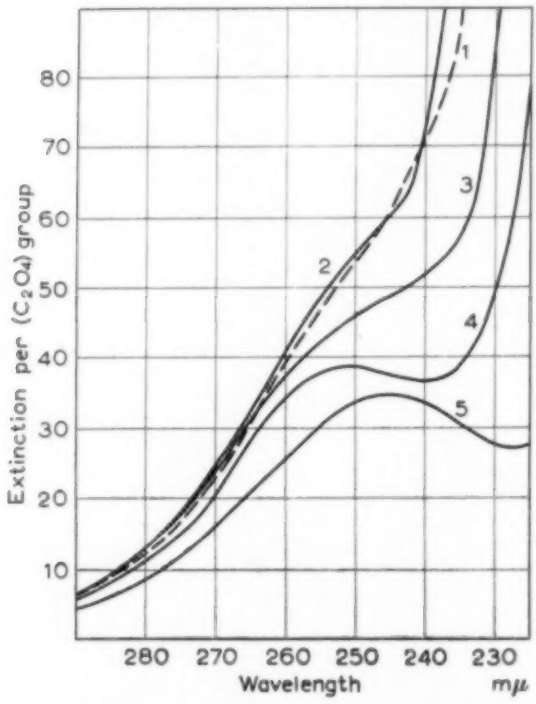


FIG. 2.—Absorption spectra of 0·01 M potassium hydrogen oxalate in water (1);
0·01 M oxalic acid in water (2);
0·01 M oxalic acid in 0·1 M HCl (3);
0·01 M oxalic acid in 1 M HCl (4)
0·01 M oxalic acid in 93% $H_2SO_4$ (5).

ion are both negligible. The absorption curve was almost identical with that of 0·01 molar aqueous oxalic acid, showing an inflexion about 250 m$\mu$ (Fig. 2).

There are thus three types of absorption curve characteristic of oxalic acid or its simple derivatives:

(1) A band of low intensity about 250 m$\mu$ appearing as a shoulder on a band of high intensity extending into the far ultra-violet, observed in methyl oxalate and molecular oxalic acid, that is in molecules in which the carboxyl group is covalently bound.

(2) A high-intensity absorption in the far ultra-violet without accompanying low-intensity band, characteristic of the oxalate ion, $(C_2O_4)^{2-}$.

(3) An absorption curve with an inflexion about 250 m$\mu$, probably due to masking

of the low-intensity band by a shift or broadening of the high-intensity band; characteristic of the $(HC_2O_4)^-$ ion in which one carboxyl group only is covalently bound to hydrogen.

1.2. *Complex oxalates in which the metallic ion has an inert-gas structure.*

Complex oxalates of beryllium $Be(C_2O_4)_2^{2-}$, aluminium $Al(C_2O_4)_3^{3-}$, and zirconium, $Zr(C_2O_4)_4^{4-}$, are stable in dilute aqueous solutions; those of magnesium,

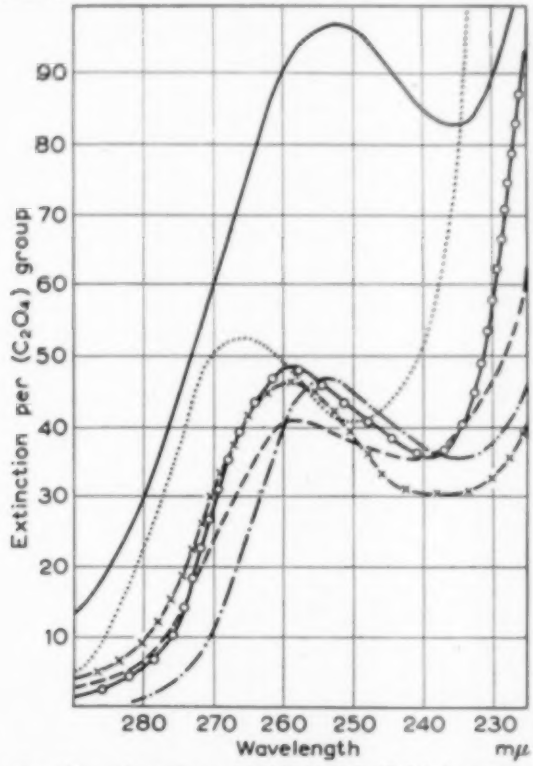


FIG. 3.—Absorption spectra of 0·0158 M $K_2Be(C_2O_4)_2$ in water – – – – – –;
0·00212 M $K_2Mg(C_2O_4)_2$ in 0·02 M $K_2C_2O_4$ –·–·–·–·–·–;
0·00268 M $K_2Al(C_2O_4)_3$ in water –×–×–×–;
0·00595 M $K_4Zr(C_2O_4)_4$ in water · · · · · ·;
0·00155 M $K_4Th(C_2O_4)_4$ in 0·02 M $K_2C_2O_4$ –o–o–o–o–o–;
0·000255 M $K_2Cu(C_2O_4)_2$ in 0·04 M $K_2C_2O_4$ ————
(this curve has the extinction reduced × 1/25).

$Mg(C_2O_4)_2^{2-}$, and thorium, $Th(C_2O_4)_4^{4-}$, are stable in aqueous solution only in the presence of excess oxalate ion. Experiments with the first three showed that the presence of excess potassium oxalate did not affect the absorption of the complex oxalates, but the use of a similar solution of potassium oxalate as comparator restricted the observation of absorption by the complexes to wavelengths above about 225 m$\mu$. The absorption spectra of all the above complexes were found to resemble those of methyl oxalate and molecular oxalic acid, a low-intensity band appearing in the region 250–270 m$\mu$, the wavelength of maximum absorption in this band varying from one complex to another (Fig. 3).

The low-intensity band thus appears to be displaced to longer wavelengths by co-ordination of the oxalate group to a metal cation; the extent of the displacement depending upon the size and valency of the cation in the ratio $Z/d^2$ approximately, where $Z$ is the valency of the cation and $d$ is the "ideal" covalent bond distance from metal atom to oxygen (in ångströms):

| oxalate | $CH_3$ | H | Mg | Be | Th | Al | Zr |
|---|---|---|---|---|---|---|---|
| $\varepsilon$ | 51 | 38 | 46 | 40 | 47 | 45 | 52 |
| $\lambda$ | 246 | 250 | 254 | 258 | 259 | 260 | 266 |
| $Z/d^2$ | — | — | 0·44 | 0·62 | 0·67 | 0·70 | 0·78 |

1.3. *Complex oxalates in which the metallic cation has a complete inner shell of d electrons*

The complex oxalates of zinc, $Zn(C_2O_4)_2^{2-}$, cadmium, $Cd(C_2O_4)_2^{2-}$, mercury, $Hg(C_2O_4)_2^{2-}$, and indium, $In(C_2O_4)_2^{-}$, have been examined. All are stable, in dilute aqueous potassium oxalate solution; the absorption spectra of these solutions showed low-intensity bands in the region 250–260 m$\mu$, displaced to longer wavelengths in a similar manner to the previous group:

| oxalate | Hg | Cd | Zn | In | Be |
|---|---|---|---|---|---|
| $\lambda_{min}$ | | 233 | 232 | 233 | 243 |
| $\varepsilon_{min}$ | | 25 | 0 | 14 | 34 |
| $\varepsilon_{max}$ | 670 | 57 | 73 | 50 | 40 |
| $\lambda_{max}$ | 253 | 255 | 257 | 258 | 258 |
| $Z/d^2$ | 0·41 | 0·41 | 0·48 | 0·61 | 0·62 |

A remarkable feature of the absorption spectra of this group of complexes was the much enhanced separation of the bands of low and high intensity, accompanied by an increase in extinction of the low-intensity bands. The improved separation was immediately apparent in the absorption curves (Fig. 4) and in the values of minimum extinction in the above table, the separation of the bands being complete (or nearly so) in the zinc and mercury complexes. In these cases the increase in extinction of the low-intensity band was most marked, especially in the mercury complex, for which the extinction was increased about fifteenfold. The reason for the greatly increased extinction of the mercury complex is not clear, but is probably related to the unusual behaviour of the 6*s* electron-pair in the mercuric ion.

An even greater increase in extinction was observed in the cupri-oxalate complex, $Cu(C_2O_4)_2^{2-}$, the shape of the absorption curve in this case resembling that of the

first group of complexes (Fig. 3). The absorption maximum at 252 m$\mu$ follows the dependence on the valency and size of the cation ($Z/d^2 = 0{\cdot}42$), and the great increase in extinction ($\varepsilon = 2400$) is again associated with a peculiarity in the electronic structure of the metal atom.

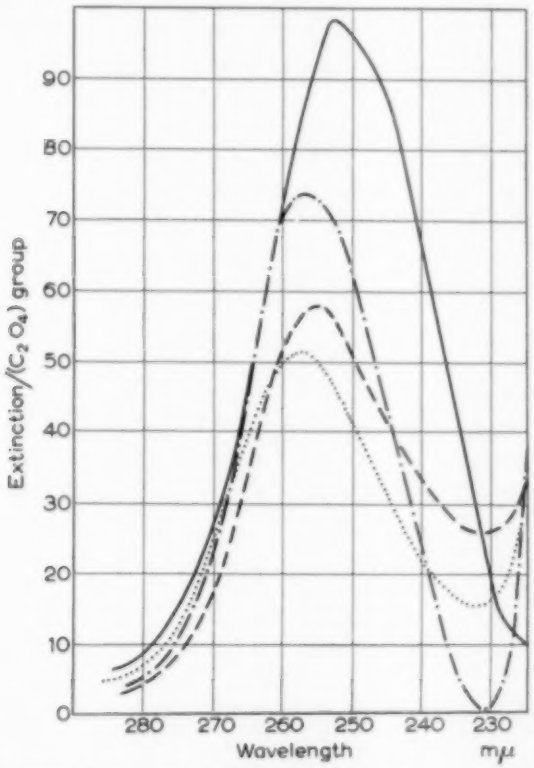


FIG. 4.—Absorption spectra of 0·00187 M $K_2Zn(C_2O_4)_2$ in 0·2 M $K_2C_2O_4$ –·–·–·–; 0·00104 M $K_2Cd(C_2O_4)_2$ in 0·04 M $K_2C_2O_4$ – – – – – –; 0·00216 M $KIn(C_2O_4)_2$ in 0·04 M $K_2C_2O_4$ · · · · · ·; 0·00159 M $K_2Hg(C_2O_4)_2$ in 0·04 M $K_2C_2O_4$ ————; (this curve has the extinction reduced × 1/7)

### 1.4. *Complexes of transition metal cations and cations with an inert pair of s electrons*

Two other important groups of complex-forming cations are those of the *B*-sub-group metals in their lower valency states (inert-pair ions) and those of the transition metals. In the latter group the partially filled shell of *d* electrons leads to absorption of light by the metal atom which may obscure absorption by co-ordinated groups. Thus the absorption spectra of oxalate complexes of trivalent chromium and cobalt observed by MEAD[4] are characteristic of the metal atoms in the complexes rather than the oxalate groups. The absorption of the ferri-oxalate ion, $Fe(C_2O_4)_3^{3-}$, was determined and also found to be characteristic of the metal atom (Fig. 6).

The absorption of aqueous solutions of the salts of divalent transition metals is usually slight in the region of 250 m$\mu$ and it seemed possible that absorption by the

[4] A. MEAD *Trans. Faraday Soc.* **30**, 1052 (1934).

oxalate complexes of these ions might be characteristic of the co-ordinated groups. The oxalate complexes, $M(C_2O_4)_2^{2-}$, of divalent manganese, cobalt, and nickel were stable in dilute aqueous potassium oxalate solution. The absorption spectra of these solutions showed no low-intensity bands in the ultra-violet, intense absorption occurring at wavelengths longer than 250 m$\mu$ and extending into the far ultra-violet; a partial exception was the absorption curve of the manganese complex, which showed

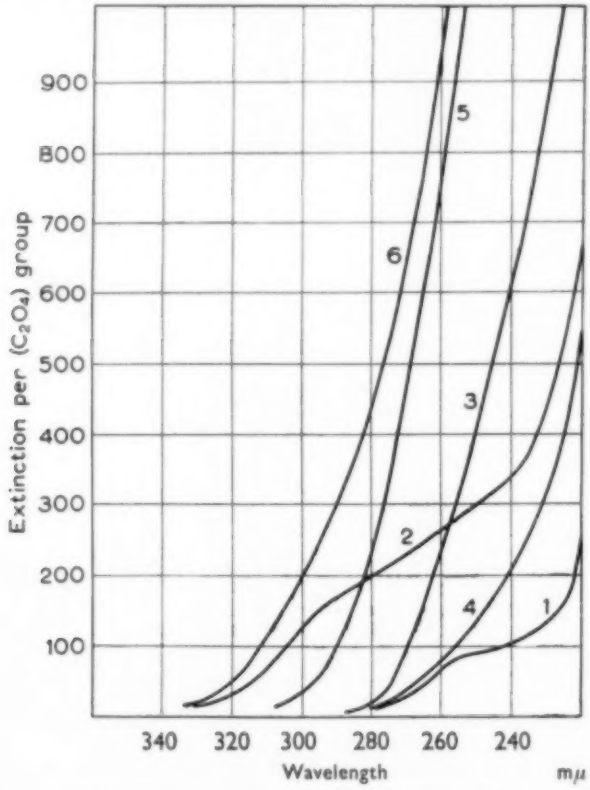


FIG. 5.—Absorption spectra of aqueous potassium oxalate solutions of $K_2Mn(C_2O_4)_2$ (1); $K_2Co(C_2O_4)_2$ (2); $K_2Ni(C_2O_4)_2$ (3); $K_2Sb(C_2O_4)_3$ (4); $K_6Sn_2(C_2O_4)_5$ (5); and $K_2TiO(C_2O_4)_2$ (6).

an inflexion about 250 m$\mu$, intense continuous absorption beginning a slightly shorter wavelength (Fig. 5).

The complexes of trivalent antimony, $Sb(C_2O_4)_3^{3-}$, and divalent tin, $Sn_2(C_2O_4)_5^{6-}$, are also stable in dilute aqueous potassium oxalate solution; the absorption spectra of these solutions showed no low-intensity bands.

## 2. ABSORPTION IN THE INFRA-RED

Absorption in the infra-red attributable to the C=O stretching vibrations normally occurs with a frequency in the region 1700–1750 $cm^{-1}$ for the esters of carboxylic acids and in the region 1600–1650 $cm^{-1}$ for their salts, a clear distinction being observed

between carboxyl groups linked to neighbouring atoms by covalent and ionic bonds. The frequency of this absorption band has been determined for methyl oxalate, potassium oxalate, and a number of complex oxalates in the solid state in suspension in "nujol." In some cases the absorption frequency has been redetermined after removal of water of crystallization by heating at 100°C *in vacuo*. The results are shown in the following table:

| Formula of oxalate | Absorption frequencies | | Abs. frequencies after heating |
|---|---|---|---|
| $K_2C_2O_4 \cdot H_2O$ | 1650 | 1628 | |
| $(CH_3)_2C_2O_4$ | 1732 (broad) | | |
| $K_2Be(C_2O_4)_2$ | 1728 | 1704 | |
| $K_3Al(C_2O_4)_3 \cdot 3H_2O$ | 1730 | 1704 | |
| $K_2Mg(C_2O_4)_2 \cdot 2H_2O$ | 1653 (broad) | | |
| $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ | 1610 (broad) | | *c.* 1600 (very broad) |
| $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ | 1673 | 1640 (sh.) | 1673 1640 |
| $K_2Mn(C_2O_4)_2 \cdot 2H_2O$ | 1635 (broad) | | 1635 (broad)* |
| $K_2Ni(C_2O_4)_2 \cdot 6H_2O$ | 1635 (broad) | | 1640 (broad)* |
| $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ | 1719 | 1685 | |
| $K_2Sb(C_2O_4)_2 \cdot 3H_2O$ | 1715 (sh.) | 1650 (broad) | *c.* 1640 (very broad) |

Sh. = shoulder *dehydration incomplete.

## 3. DISCUSSION OF RESULTS

### 3.1. *Type of bond linking the oxalate group to the co-ordinating metal cation*

Magnetic susceptibility measurements indicate that cations of transition metals are able to form two types of co-ordination complex, designated covalent and ionic by PAULING,[5] who, however, recognized that the latter term might be misleading. It is now generally thought that the bonds in these ionic complexes are in fact covalent, but that higher *d* orbitals of the metal cation are used in the formation of the hybrid-bond system, leaving unpaired electrons in the lower *d* orbitals to give the complex magnetic properties similar to those of the unco-ordinated cation. Magnetic evidence is thus unable to distinguish between a complex in which the cation is bound covalently by bonds of this "outer-orbital" type and the cation itself. Evidence based on chemical reactions or reactivity is necessarily circumstantial, as it refers rather to the nature of excited transition states. Absorption spectrography, however, provides a direct means of observing the internal structure of a molecule or ion when it is only slightly excited, and should make it possible, at least in some cases, to distinguish between "outer orbital" complexes and those in which the bonding within the complex is truly ionic.

The ultra-violet absorption spectra of potassium oxalate and methyl oxalate and of oxalic acid in aqueous solutions of varying acidity show that an absorption band of low intensity about 250 m$\mu$ is characteristic of the covalently bound oxalate group. This absorption band is observed in the spectra of the oxalate complexes of beryllium, magnesium, aluminium, zirconium, thorium, zinc, cadmium, and indium, and with greatly increased intensity in those of the mercuric and cupric complexes. All these

[5] L. PAULING *The Nature of the Chemical Bond*, 112–23, Cornell University Press, New York (1942).

complexes must be considered to have metal-oxalate linkages of a truly covalent character, the hybrid bond systems involved being probably as follows:

| | | |
|---|---|---|
| tetrahedral | Be | $2s2p^3$ |
| | Mg | $3s3p^3$ |
| | Zn | $4s4p^3$ |
| | Cd | $5s5p^3$ |
| | $Hg^{II}$ | $6s6p^3$ |
| planar | $Cu^{II}$ | $3d4s4p^3$ "inner-orbital" |
| octahedral | Al | $3s3p^33d^2$ "outer-orbital" |
| cubic | Zr | $4d^45s5p^3$ "inner-orbital" |
| | Th | $6d^47s7p^3$ "inner-orbital" |

It may be noted that only in the aluminium complex is there no alternative to "outer-orbital" co-ordination, but as the aluminium complex is one of the most stable, at least towards hydrolysis, "outer-orbital" co-ordination cannot be excluded for the zirconium and thorium complexes.

Support for the covalent nature of the co-ordinate linkages in the beryllium and aluminium complexes is provided by the frequencies of the C=O stretching fundamentals (1704–1730 $cm^{-1}$), which are similar to those observed in methyl oxalate (1732 $cm^{-1}$) and other esters. The absorption of the magnesium complex in the ultra-violet is so similar to that of the aluminium and beryllium complexes that it may be taken as clear evidence of the covalency of the co-ordinate linkages, although the much lower C=O stretching frequency observed (1653 $cm^{-1}$) is suggestive of ionic bonding; however, an accompanying shift to lower frequency of the absorption in the 3 $\mu$ region, attributable to water of crystallization (3420 $cm^{-1}$ in the aluminium complex, 3250 $cm^{-1}$ in the magnesium complex), indicates the formation of strong hydrogen bonds in the hydrated crystalline magnesium complex. The formation of such bonds is also suggested by the impossibility of dehydrating the magnesium complex without decomposition. It is also possible that the strongly attached water is directly co-ordinated to the magnesium, leading to an octahedral complex of the form $Mg(OH_2)_2(C_2O_4)_2^{2-}$.

The absorption frequencies of the C=O groups in the oxalate complexes of cadmium and copper are also considerably lower than in the beryllium and aluminium complexes, and the absorption bands are broad. It thus appears that the absorption of the C=O group in the infra-red is often unsatisfactory as a criterion of bond type, probably due to hydrogen-bond formation, which cannot be avoided when the hydrated crystalline complex salts are examined. The possibility must also be considered that the co-ordinate linkages may in some cases be ionic in the solid state but covalent in aqueous solutions.

The ultra-violet absorption of the oxalate complexes of divalent transition metals is heavy in the region of 250 m$\mu$ (Fig. 5), so that the low-intensity band characteristic of covalently bound oxalate groups cannot be observed, although an inflexion about 250 m$\mu$ in the absorption curve of the manganese complex suggests that this band is in fact present. The C=O stretching absorptions of the manganese and nickel complexes appear as broad bands about 1635 $cm^{-1}$; as with the magnesium complex, water of crystallization is retained very strongly and strong hydrogen-bonds are probably responsible for shifts of the absorption to lower frequencies. Assuming that the metal-oxalate linkages are in fact covalent in these complexes, it may be noted that

the shift of the infra-red absorption to lower frequencies occurs in those hydrated crystals in which the co-ordination number of the metal is not satisfied by the number of oxalate groups co-ordinated. The absorption of the antimony complex, $Sb(C_2O_4)_3^{3-}$, in the infra-red shows a distinct shoulder at a frequency of 1716 $cm^{-1}$, though in the ultra-violet both this and the stannous complex, $Sn_2(C_2O_4)_5^{6-}$, absorb at wavelengths long enough to obscure the 250 m$\mu$ region. The evidence in respect of this group of complex oxalates must, however, be considered inconclusive.

The ferrioxalate ion, $Fe(C_2O_4)_3^{3-}$, is one of the best known examples of an "ionic" or "outer-orbital" complex. The weakness of the iron-oxalate linkages is shown by the fairly rapid hydrolysis of the complex in water and by its rapid exchange with labelled oxalate ions. The complex oxalates, $M(C_2O_4)_3^{3-}$, of aluminium, chromium, and cobalt are stable in aqueous solution, but the "outer-orbital" aluminium complex exchanges rapidly with labelled oxalate ions, whereas the "inner-orbital" chromium and cobalt complexes exchange very slowly.[6, 7] The covalent nature of the iron-oxalate bonds is shown by the frequencies of the C=O stretching fundamentals at 1719 and 1685 $cm^{-1}$. In the ultra-violet the ferrioxalate ion absorbs heavily below 350 m$\mu$. The absorption spectra of ferric salts are of particular interest, as the absorption curves (which are characteristic of the iron atom rather than the co-ordinated groups) form an obviously related series, irrespective of whether the co-ordination is of the "inner orbital" ($CN^-$, $CNS^-$) or the "outer-orbital" ($OH_2$, $C_2O_4^{2-}$) type (Fig. 6). This intense absorption at longer wavelengths probably represents charge transfer processes of the type

$$A^{-x} + M^{+y} = A^{-(x-1)} + M^{+(y+1)}.$$

The intense absorption observed in the oxalate complexes of the oxidizing cations $Cu^{++}$ and $Hg^{++}$ may also be due to such processes; but if this were so, we should expect absorption to occur, in these cases also, at wavelengths quite unrelated to those at which the normal oxalate complexes absorb.

Examination of ultra-violet and infra-red absorption by complex oxalates thus provides satisfactory evidence of the covalence of the metal-oxalate bonds in the cases where the cation is trivalent iron or has an inert-gas structure (beryllium, magnesium, aluminium, zirconium, thorium) or a structure with a complete inner shell of *d* electrons (zinc, cadmium, indium, divalent mercury). There is less conclusive evidence of covalency in the complexes of divalent copper and manganese (ultra-violet) and trivalent antimony (infra-red), but examination of the oxalate complexes of divalent iron, cobalt, nickel, and tin was inconclusive.

### 3.2. *Wavelength of the low-intensity band*

The low-intensity band, characteristic of covalently bound oxalate groups is displaced to longer wavelengths as the coulombic attractive force between the metal cation and the co-ordinated oxalate group increases. The wavelength of the absorption band represents an electronic transition energy, probably of the $\pi$-electrons in the C=O groups. This energy ($E$) may thus be represented:

$$E = E_0 + \Delta E$$

where $E_0$ is a fundamental transition energy and $\Delta E$ is a variable component

[6] F. A. Long *J. Amer. Chem. Soc.* **61**, 570 (1939); ibid. **63**, 1353 (1941).
[7] H. C. Clark, N. F. Curtis and A. L. Odell *J. Chem. Soc.* 63 (1954).

attributable to the influence of the co-ordinating cation. The experimentally determined values of $E$ are related to the properties of the co-ordinating cation by the equation

$$E = -k\frac{Z}{l^2} \tag{1}$$

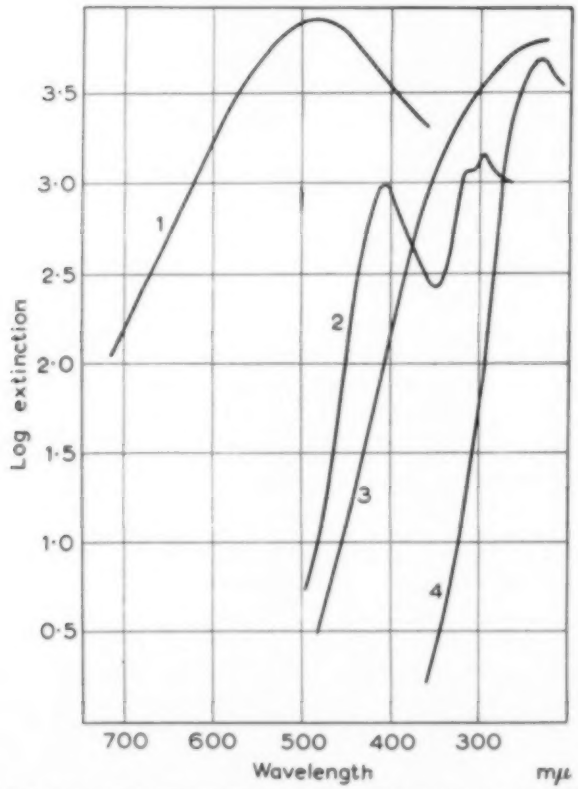


FIG. 6.—Absorption spectra of aqueous $Fe(SCN)_3$[8] (1); $K_3Fe(CN)_6$[8] (2); $K_3Fe(C_2O_4)_3$ in aqueous $K_2C_2O_4$ (3); and $Fe(ClO_4)_3$ in aqueous $HClO_4$[8] (4).

where $Z$ = valency of the cation, $l$ = the distance of the cation from the carbonyl groups (see note b), and $k$ is a proportionality constant. It may be noted that if methyl oxalate and oxalic acid are regarded as complexes in which the oxalate ion is co-ordinated to $CH_3^+$ or $H^+$, the absorption wavelengths of these substances obey the same relationship (Fig. 7).

It is of interest to attempt a theoretical calculation of the effect of a nearby cation upon the transition energy of an electron. A calculation of this type has been recently made by BELFORD, MARTELL, and CALVIN, using molecular orbital theory to account for the shift of the high-intensity absorption band of acetyl acetone when co-ordinated to copper.[9] For the present purpose a simpler approach will be made on the basis of classical electrostatics, considering the transition of the electron as taking place in

[8] A. KISS, J. ABRAHAM, and I. HEGEDUS *Z. anorg. Chem.* **244**, 98 (1940).
[9] R. L. BELFORD, A. E. MARTELL, and M. CALVIN *J. Inorg. Nucl. Chem.* **2**, 11 (1956).

space (rather than energy) under the influence of simple coulombic forces. A simplification of this sort is in any case necessary, as the geometry of the system varies from one complex to another and is not known exactly.

This approach gives the familiar expression for the fundamental transition energy of an electron of the form

$$E_0 = e_1 e_2 \left\{ \frac{1}{r_1} - \frac{1}{r_2} \right\} \tag{2}$$

where $e_1$ and $e_2$ are the charges on the electron and the retaining atom and $r_1$ and $r_2$ the distances of the electron from this atom before and after transition. Similarly the

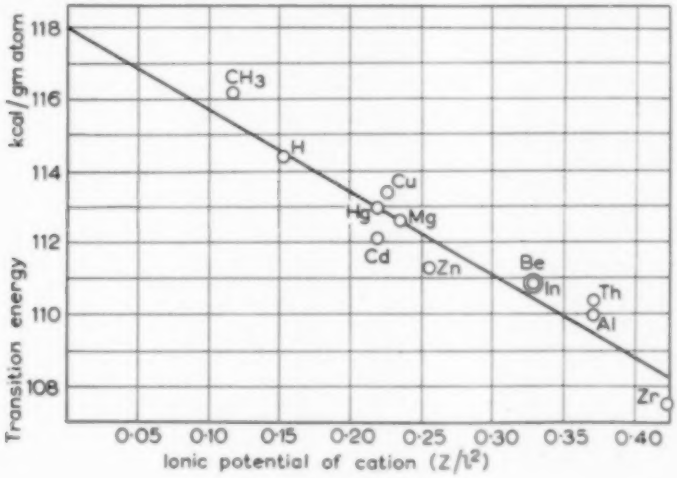


FIG. 7.

component of transition energy due to the attractive effect of the neighbouring cation is given by the expression

$$\Delta E = Z e_1 \left\{ \frac{1}{l_2} - \frac{1}{l_1} \right\} \tag{3}$$

where $Z$ is the valency (charge) of the cation and $l_1$ and $l_2$ the distances of the electron from the cation before and after transition

From equation (2)

$$E_0 = e_1 e_2 \left\{ \frac{r_2 - r_1}{r_1 r_2} \right\}$$

whence

$$r_2 - r_1 = \frac{E_0 r_1 r_2}{e_1 e_2}$$

and from equation (3)

$$\Delta E = Z e_1 \frac{l_1 - l_2}{l_1 l_2}$$

but since $r_2 - r_1 = -(l_2 - l_1)$, it follows that

$$\Delta E = -\frac{Z e_1}{l_1 l_2} \times \frac{E_0 r_1 r_2}{e_1 e_2}$$

and as $r_2 - r_1$ is small compared with $r_2$ or $r_1$, the product $r_1r_2$ may be replaced by $r^2$, where $r$ is the mean of $r_1$ and $r_2$; $l_1l_2$ may similarly be replaced by $l^2$, giving

$$\frac{\Delta E}{E_0} = -\frac{Z}{e_2} \times \frac{r^2}{l^2}.$$

For the effect of a variety of neighbouring cations on a common electronic transition, $E_0$, $r$, and $e_2$ are constants, whence

$$E = -k\frac{Z}{l^2} \tag{4}$$

identical with the experimentally obtained relation of equation (1). In this equation the constant $k$ is now given by

$$k = \frac{E_0 r^2}{e_2}$$

and can be evaluated as follows. $E_0$ is determined graphically (Fig. 7) = 118 kcal/gm-atom; $r$ is the distance of a bonding electron in the C═O group of the oxalate ion from the retaining atoms, this distance is of the order of half the C═O bond length or about 0·6 Å; $e_2$ is the charge resisting electronic transition and for an electron attached to an uncharged atom will be equal to one electronic charge, whence $k = 42$, where $\Delta E$ is in kcal/gm-atom, $Z$ is in electronic units, and $l$ in ångströms. Considering the unavoidable approximation made in the value of $r$, this is in remarkably good agreement with the experimentally determined value of $k = 24$.

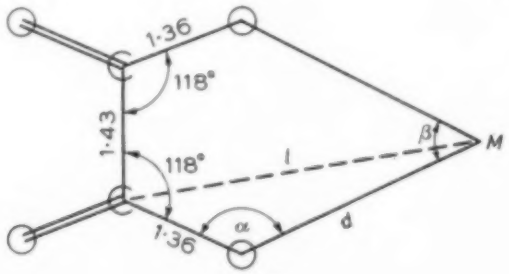


FIG. 8.

*Note (a)—Calculation of the approximate value of* $r_2 - r_1$

Numerical values of $r_1$ and $r_2$ are not known and have no real meaning for the transition of a $\pi$-electron of a double bond, but it is important that $r_2 - r_1$ should be comparatively small, and an attempt at calculation of $r_2 - r_1$ is made as follows. From equation (2)

$$r_2 - r_1 = \frac{E_0 r^2}{e_1 e_2}$$

using $r^2$ as an approximation to the product $r_1r_2$. Inserting the numerical values used above

$$E_0 = 118 \text{ kcal/g-atom} = \frac{118 \times 4{\cdot}184 \times 10^{10}}{6{\cdot}02 \times 10^{23}} \text{ ergs/atom}$$

$$r = 0{\cdot}6 \text{ Å} = 6 \times 10^{-9} \text{ cm}$$

$$e_1 = e_2 = 4{\cdot}803 \times 10^{-10} \text{ e.s.u.}$$

whence $r_2 - r_1 = 1{\cdot}3 \times 10^{-9}$ cm = 0·13 Å, which is a reasonable result.

*Note (b)—Calculation of l in equation* (1)

Fig. 8 shows a single oxalate group co-ordinated to the metal M. The bond lengths and angles are based on the values observed in crystalline oxalic acid dihydrate[10] and the vapours of methyl formate

[10] J. M. ROBERTSON and I. WOODWARD *J. Chem. Soc.* 1817 (1936).

and acetate.[11] The distance $l$ is the shortest between the metal atom and the carbonyl group and has been calculated assuming that the oxalate group is rigid and planar and the distance $d$ is the sum of the "ideal" covalent radii of the atoms M and O. The most serious source of inaccuracy is probably in the assumption of rigidity of the oxalate group. The co-ordination angle $\beta$, which should be 109·5° for tetrahedral co-ordination, 90° for octahedral, and 70·5° for 8: co-ordination, is consistent with the other bond lengths and angles only in one case (the zirconium complex) and in the others the discrepancy is no doubt spread over the whole ion.

In order to include oxalic acid and methyl oxalate in the series of covalent oxalates, the distance $l$ has been calculated for these molecules assuming angles at $\alpha$ of 112° for methyl oxalate and 107° for oxalic acid. The following table shows the calculated values for $l$ and $Z/l^2$ and also the observed wavelengths of the absorption maxima and derived energies of transition.

| M | $Z$ | co-ord. number | $r_{cov}$ (Å) | $l$ (Å) | $\frac{Z}{l^2}$ | $\lambda$ (mμ) | $E$ (kcal) |
|---|---|---|---|---|---|---|---|
| H | 1 | 1 | 0·37 | 2·56 | 0·153 | 250 | 114·4 |
| $CH_3$ | 1 | 1 | 0·77 | 2·93 | 0·117 | 246 | 116·2 |
| Be | 2 | 4 | 1·06 | 2·47 | 0·328 | 258 | 110·9 |
| Mg | 2 | 4 | 1·40 | 2·93 | 0·234 | 254 | 112·6 |
| Al | 3 | 6 | 1·34 | 2·85 | 0·370 | 260 | 110·0 |
| Zr | 4 | 8 | 1·53 | 3·08 | 0·422 | 266 | 107·5 |
| Th | 4 | 8 | 1·70 | 3·28 | 0·371 | 259 | 110·4 |
| $Cu^{II}$ | 2 | 4 square | 1·44 | 2·98 | 0·225 | 252 | 113·4 |
| Zn | 2 | 4 | 1·31 | 2·81 | 0·254 | 257 | 111·3 |
| Cd | 2 | 4 | 1·48 | 3·03 | 0·218 | 255 | 112·1 |
| $Hg^{II}$ | 2 | 4 | 1·48 | 3·03 | 0·218 | 253 | 113·0 |
| In | 3 | 4 | 1·48 | 3·03 | 0·328 | 158 | 110·9 |

## 4. EXPERIMENTAL

*Complex oxalates were prepared*: (1) by precipitating an aqueous solution of a salt of the metal by potassium oxalate, filtering the precipitate, and dissolving it in a slight excess of hot concentrated potassium oxalate solution, from which the complex oxalate crystallized on cooling; (2) by heating the oxide or hydroxide of the metal in a solution containing the theoretically required amount of oxalic acid and a slight excess of potassium oxalate, the complex oxalate crystallizing on cooling.

The compositions of the complexes were checked by titration with standard potassium permanganate in hot dilute sulphuric-acid solution. The methods of preparation and analyses of the complex salts examined were as follows.

Aluminium potassium oxalate, (2); found 57·8% $C_2O_4$. $K_3Al(C_2O_4)_3 \cdot 3H_2O$ requires 57·1%.

Antimony potassium oxalate, (2); antimony was estimated iodimetrically and antimony and oxalate together by permanganate; found 22·0% Sb, 46·8% $C_2O_4$; $K_3Sb(C_2O_4)_3 \cdot 3H_2O$ requires 21·9% Sb, 47·4% $C_2O_4$.

Beryllium potassium oxalate (2); found 66·8% $C_2O_4$; $K_2Be(C_2O_4)_2$ requires 66·8%.

Cadmium potassium oxalate, (1); found 42·2% $C_2O_4$; $K_2Cd(C_2O_4)_2 \cdot 3H_2O$ requires 41·9%.

Cobalt potassium oxalate, (1); found 42·2% $C_2O_4$; $K_2Co(C_2O_4)_2 \cdot 6H_2O$ requires 41·6%; pink.

Cupric potassium oxalate, (1); found 50·0% $C_2O_4$; $K_2Cu(C_2O_4)_2 \cdot 2H_2O$ requires 49·8%; blue.

Ferric potassium oxalate (commercial sample recrystallized from dilute potassium-oxalate solution); found 53·5% $C_2O_4$; $K_3Fe(C_2O_4)_3 \cdot 3H_2O$ requires 53·7%; green.

Indium potassium oxalate, (2); found 45·9% $C_2O_4$; $KIn(C_2O_4)_2 \cdot 3H_2O$ requires 45·8%.

Magnesium potassium oxalate, (1); found 56·2% $C_2O_4$; $K_2Mg(C_2O_4)_2 \cdot 2H_2O$ requires 56·2%.

[11] J. M. O'Gorman, Wm. Shand, and V. Schomaker *J. Amer. Chem. Soc.* **72**, 4222 (1950).

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Manganese potassium oxalate, (1); found 50·9% $C_2O_4$; $K_2Mn(C_2O_4)_2 \cdot 2H_2O$ requires 51·0%, pale pink.

Mercuric potassium oxalate, (2); found 35·4% $C_2O_4$; $K_2Hg(C_2O_4)_2 \cdot 2H_2O$ requires 35·8%.

Nickel potasssium oxalate, (1); found 42·1% $C_2O_4$; $K_2Ni(C_2O_4)_2 \cdot 6H_2O$ requires 41·6%; green.

Stannous potassium oxalate, (1); stannous ion was estimated iodimetrically and stannous and oxalate together by permanganate; found 24·5% Sn, 46·2% $C_2O_4$; $K_4Sn_2(C_2O_4)_5 \cdot 3H_2O$ requires 24·7% Sn, 45·6% $C_2O_4$.

Thorium potassium oxalate, (1); found 47·5% $C_2O_4$; $K_4Th(C_2O_4)_4 \cdot 4H_2O$ requires 47·5%.

Titanium potassium oxalate (commercial sample recrystallized from dilute potassium oxalate solution); found 47·6% $C_2O_4$; $K_2TiO(C_2O_4)_2 \cdot 3H_2O$ requires 47·4%.

Zinc potassium oxalate, (1); found 52·1% $C_2O_4$; $K_2Zn(C_2O_4)_2 \cdot H_2O$ requires 52·1%.

Zirconium potassium oxalate (commercial sample recrystallized from water); found 53·2% $C_2O_4$; $K_4Zr(C_2O_4)_4 \cdot 4H_2O$ requires 52·5%.

*Ultra-violet absorption spectra* were determined in a Unicam SP500 photoelectric absorptiometer with manual operation. 1-cm quartz cells were used and readings of absorption density normally taken at intervals of 5 m$\mu$ except over the peaks of absorption bands, where the intervals were reduced to 1 m$\mu$.

*Infra-red absorption spectra* of the crystalline complex oxalates in suspension in "nujol" were determined by Dr. L. A. DUNCANSON of the I.C.I. Akers Research Laboratories, Welwyn, to whom the author expresses his thanks.

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# LETTERS TO THE EDITORS

## Purification of Plutonium by a Cation Exchanger

(*Received* 27 *April* 1956; *in final form* 9 *July* 1956)

After a 30-month cooling period, uranium from JEEP containing approximately 5 mg plutonium per kg, was dissolved in nitric acid. Small portions of a solution 6 M in nitric acid and 1·9 M in uranium were extracted with a mixture of 30 vol.% tri-n-butyl phosphate and 70 vol% kerosene.* Washing the organic layer with 3 M nitric acid 0·1 M in sodium nitrite† and stripping the plutonium with a hydrazine solution, resulted in a solution 1 M in nitric acid, $3{\cdot}2 \times 10^{-2}$ M in uranium, 0·23 M in hydrazine, $2{\cdot}8 \times 10^{-6}$ M in plutonium and containing approx. 3000 c.p.m. beta activity per ml. The subsequent purification procedure was still able to deal with such a concentration of uranium.

Table 1. Break-through and total capacities for the $N_2H_5^+$-ion at different pH values. Hydrazine concentration 0·10 N. Dowex 50 [$H^+$, 160–200 mesh], air dried.

| pH | Break-through capacity in meq./g | Total capacity in meq./g |
|---|---|---|
| 0·20 | 1·90 | 1·96 |
| 0·50 | 2·17 | 2·25 |
| 1·00 | 2·60 | 2·68 |
| 1·80 | 3·18 | 3·32 |
| 3·10 | 3·60 | 3·90 |

The purification of the plutonium in this solution by Dowex 50 was studied in order to avoid a pH-sensitive precipitation as described by Goldschmidt *et al.*[1] Break-through and total capacities for the $N_2H_5^+$-ion at different pH values were determined and are listed in Table 1.

As little hydrazine as possible has to be retained on the resin, so a low pH value has to be chosen. A rather low choice does not influence the $Pu^{3+}$ adsorption appreciably, but the adsorption of $UO_2^{++}$ is affected much more, as is shown in Fig. 1. This figure gives break-through curves for 0·3 M hydrazine—0·005 M uranyl nitrate solutions at some pH values. Elution of resin, saturated with hydrazine and uranium and containing some plutonium, with 1·5 M nitric acid resulted in a good separation of the plutonium from the hydrazine and the uranium. In order to avoid a possible contamination of plutonium with organic material originating from decomposition of the resin by nitric acid, elution with 1·5 M hydrochloric acid was also performed. A slightly faster elution of plutonium was found in this case.

Based on these results a separation method for the plutonium from the solution obtained in the extraction procedure was worked out.

50 ml of this solution were diluted with water to pH 0·27 and passed through a column filled with

* We are grateful to Mr. B. Aabakken who built the apparatus and performed the extractions.

† D. H. W. den Boer and Z. I. Dizdar, to be published.

[1] B. Goldschmidt, P. Regnaut, and I. Prevot *International Conference on the Peaceful Uses of Atomic Energy*, Paper no. P349 (1955).

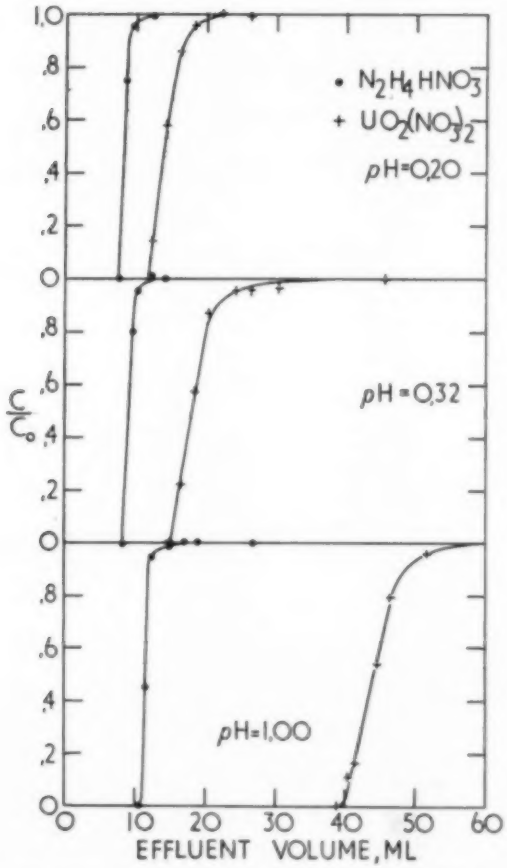


FIG. 1.—Adsorption of hydrazine and uranium(VI) on Dowex 50 at different pH values.

one gram air-dried Dowex 50 [$H^+$, 160–200 mesh] at a flow rate of 1 ml sq $cm^{-1}$ $min^{-1}$. An effluent was obtained containing 82% of the original quantity of the hydrazine and 69% of the uranium. The column was washed with 0·1 M nitric acid and eluted with 1·5 M nitric acid. The course of the elution is shown in Fig. 2. The adsorbed hydrazine and the uranium are eluted first, followed by plutonium, contaminated with some fission product activity. In this case one beta peak was obtained, while in some other experiments two beta peaks could be detected. Elution with 5 M nitric acid, performed afterwards, yields most of the adsorbed fission products. After this, however,

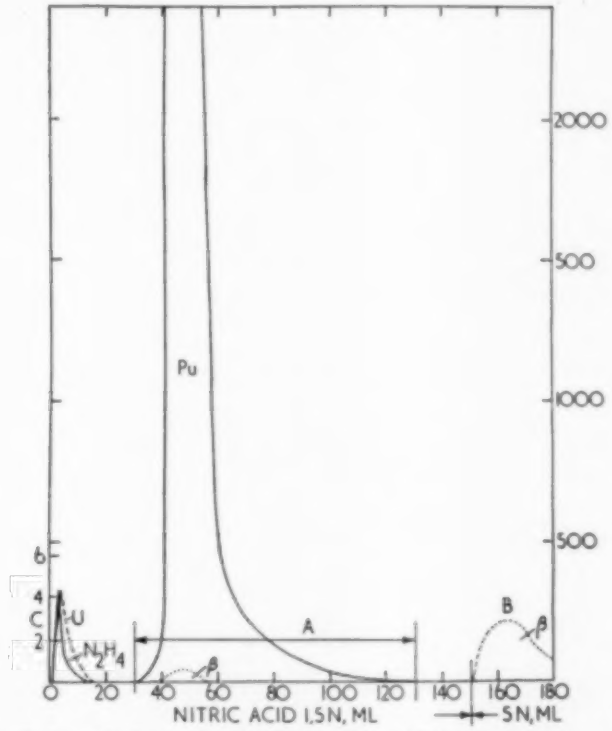


FIG. 2.—Elution of hydrazine, uranium(VI), plutonium(III) and gross fission products from Dowex 50. Ordinates: hydrazines and uranium in arbitrary units, plutonium and fission products in c.p.m./0·1 ml.

the column was still active. Concentrated hydrochloric acid, 0·5 M oxalic acid, 0·5 M sulphuric acid and 7 M nitric acid were unable to remove this activity which remained adsorbed at the top of the column. Aluminium absorption curves show that peak *B* as well as the noneluable activity was due to Ru 106-Rh 106. Evidently different valency states of ruthenium are present in the original solution, causing different affinities of this element towards the resin.

The plutonium can, if necessary, be purified further by TTA extraction[2] or other procedures.

This note is published by permission of the Director of JENER, Kjeller, Norway, one of us (Z. I. D.) being indebted to the Establishment for their kind hospitality during the work. The interest and support of Dr. T. J. BARENDREGT is gratefully acknowledged.

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[2] E. K. HYDE *National Nuclear Energy Series, Division IV*, Vol. 14-A, chap. 15, McGraw-Hill Book Co. New York (1954).

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## Totally Symmetric Vibration Frequencies of the Hexafluorophosphate-ion and Isoelectronic Species

(*Received* 29 *July* 1956)

In a letter to the editors, D. Fortnum and J. O. Edwards report[1] the Raman spectrum of the $PF_6^-$ ion in an aqueous solution of the potassium salt. The principal feature found was a line with $\Delta\nu = 750\ cm^{-1}$. In the course of unpublished Raman investigations of a number of complex ions o type $XY_6$ we had observed $\Delta\nu = 741\ cm^{-1}$ (probable limits of error $\pm 5\ cm^{-1}$) for the $PF_6^-$ ion in an approximately 2M solution of the ammonium salt. This is in fair agreement with the finding of Fortnum and Edwards. Since $PF_6^-$ is doubtless regular octahedral (point group $O_h$), the above-mentioned frequency may be assigned with confidence to the totally symmetric mode, i.e. to $\nu_1(A_{1g})$, which is expected to give the sharpest and most intense Raman line.

We prepared our ammonium hexafluorophosphate from phosphorus pentachloride and potassium bifluoride via the hexammino-cadmium salt.[2] The Raman spectrum of the aqueous solution (made very slightly acid to suppress the development of turbidity) showed a considerable background continuum, strongest in the green but extending into the blue region, which was apparently due to a trace of fluorescence, since it could be partially quenched by the addition of a very small amount of hydroquinone. The principal exciting line was Hg-4358 Å, and on account of the background the other two Raman-active frequencies, $\nu_2(E_g)$ and $\nu_5(F_{2g})$, were not discernible. The photometer curve of Fortnum and Edwards (*loc. cit.*) shows the corresponding "lines" as relatively feeble and very diffuse.

Table 1

| | $SiF_6^{2-}$ | $PF_6^-$ | $SF_6$ | $ZnBr_4^{2-}$ | $GaBr_4^-$ | $GeBr_4$ | $BH_4^-$ | $CH_4$ | $NH_4^+$ |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_1$ ($cm^{-1}$) | 656 | 741 | 775 | 172 | 210 | 234 | 2270 | 2914 | 3033 |
| Reference | 3 | | 4 | 5 | 6 | 7 | 8 | 7 | 7 |
| $10^{-5}\,k$ (dynes/cm) | 4·81 | 6·14 | 6·72 | 1·39 | 2·08 | 2·58 | 3·06 | 5·04 | 5·46 |
| $\Delta k$ (per cent) | — | 28 | 9 | — | 50 | 24 | — | 65 | 8 |

Our principal object in investigating $PF_6^-$ was to obtain the symmetric "breathing" frequency $\nu_1$, and hence the bond-stretching force constant $k$, for comparison with the corresponding values for the isoelectronic species $SiF_6^{2-}$ and $SF_6$. The results are shown in Table 1, from which it is seen that the $k$ values (calculated by using the simple valency force field) increase with increase of the atomic number of the central atom. The dependence is not linear, however: in fact, there is a considerably greater increase in going from $SiF_6^{2-}$ to $PF_6^-$ than in going from the latter to $SF_6$.

It is interesting to note that this behaviour is qualitatively similar to that pointed out by Woodward and co-workers[9, 8, 10] for isoelectronic triads of tetrahedral $XY_4$ species. Two examples are included


[1] D. Fortnum and J. O. Edwards *J. Inorg. Nucl. Chem.* **2**, 264 (1956).
[2] W. G. Palmer *Experimental Inorganic Chemistry* Cambridge University Press, p. 300 (1954).
[3] Y. K. Syrkin and M. V. Wolkenstein *Acta Physicochim. U.S.S.R.* **2**, 308 (1935)
[4] J. Gaunt *Trans. Faraday Soc.* **49**, 1122 (1953).
[5] M.-L. Delwaulle *Compt. rend.* **240**, 2132 (1955).
[6] L. A. Woodward and A. A. Nord *J. Chem. Soc.* 2655 (1955).
[7] G. Herzberg *Infra-red and Raman Spectra of Polyatomic Molecules* Van Nostrand, New York, p. 167 (1945).
[8] L. A. Woodward and H. L. Roberts *J. Chem. Soc.* 1170 (1956).
[9] L. A. Woodward and P. T. Bill *ibid* 1699 (1955). In this paper the values of $10^{-5}\,k$ should read: $CdBr_4^{2-}$, 1·30; $InBr_4^-$, 1·83; $SnBr_4$, 2·28 dynes per cm.
[10] L. A. Woodward and H. L. Roberts *Trans. Faraday Soc.* **52**, 1458 (1956). This paper deals with the triad $AlH_4^-$, $SiH_4$, $PH_4^+$.

in Table 1 for comparison. So far as we are aware, $SiF_6^{2-}$, $PF_6^-$, and $SF_6$ form the first isoelectronic triad of octahedral species to have been considered. The dependence of $k$ upon the atomic number of the central atom in this and other cases will be dealt with more fully in subsequent publications.

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## An Anion-exchanger Process for Gram-scale Separation of Americium from Rare Earths*

(*Received* 22 *October* 1956)

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WE wish to report a simple one-step process for the separation of gram amounts of americium from large quantities of light rare earths. The separation utilizes the marked tendency of a strong-base anion exchanger such as Dowex 1 to absorb americium from moderately concentrated ammonium thiocyanate solutions in preference to light rare earths. Differences in anion-exchange absorption among various 4*f* and 5*f* elements in ammonium thiocyanate solutions have been noted by DIAMOND,[1] SURLS,[2] and BARNES and SACKETT.[3]

TABLE 1

| Initial rare earth (grams) | Initial Am (grams) | Volume anion exchanger (litres) | Final rare earth impurity (g/g Am) | Am loss (grams) |
|---|---|---|---|---|
| 1·3 | 0·24 | 0·15 | <0·015 | 0·004 |
| 9 | 0·69 | 2·3 | <0·01 | 0·003 |
| 12 | 2·19 | 1·4 | <0·015 | 0·002 |
| 35 | 0·20 | 1·4 | 0·42 | 0·002 |
| 100 | 0·28 | 1·4 | 21·0 | 0·001 |
| 130 | 0·50 | 2·3 | 0·19 | 0·003 |

The process we used consisted essentially of absorption of americium from 5 M ammonium thiocyanate solution on a column of anion exchanger (Dowex 1 × 8) and continued elution with this same reagent until the rare earths had been removed. Americium was then stripped from the column using 0·1 N hydrochloric acid. A convenient method of obtaining the americium feed solution for the anion column is to absorb the americium and rare earths on the cation exchanger Dowex 50, wash with water, then strip with 5 M ammonium thiocyanate.

Some results from the six runs we have made are shown in Table 1. In separating four grams of americium from 280 grams of rare earth, we obtained 99·6% of the americium essentially free of

* This work was sponsored by the U.S. Atomic Energy Commission.

[1] R. M. DIAMOND, K. STREET JR., and G. T. SEABORG U.S. Atomic Energy Commission Report UCRL-1434.

[2] J. P. SURLS JR. U.S.A.E.C. Report UCRL-3209.

[3] J. W. BARNES and W. M. SACKETT, Los Alamos Scientific Laboratory, private communication.

rare earths. The rare earths consisted of lanthanum and cerium plus trace amounts of heavier rare earths. Spectrographic analysis of various fractions showed that the elution maxima of the heavier rare earths, including ytterbium, occurred before appreciable amounts of americium eluted. In each run we used a 40-cm-long column of thiocyanate-form anion exchanger and maintained the flow rates at about 1 $cm^3/cm^2$-min. With rare earth to americium ratios of about 300/1, about 20 ml of anion exchanger appears to be required for each gram of rare earth in order to achieve essentially complete separation, or roughly 6 milliequivalents of exchange capacity for each millimole of rare earth.

We are currently making more detailed study of the anion-exchanger absorption of various *4f* and *5f* elements from ammonium thiocyanate, including study of the variations in absorption coefficients with loading.

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T. K. Keenan, L. E. LaMar,
D. E. Armstrong, L. B. Asprey.

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J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 329 to 332. Pergamon Press Ltd., London

# ATOMIC WEIGHTS COMPUTED FROM PHYSICAL MEASUREMENTS

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(*Received* 15 *August* 1956)

**Abstract**—Chemical atomic weights are calculated from isotopic abundance ratios and earlier computations of isotopic masses.

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ATOMIC weights of elements have mainly been determined in the past by chemical methods. Progress in mass spectroscopy offered a new method for the determination of atomic weights, since the masses of isotopes and the isotopic constitutions of elements could both be measured with high precision. Therefore, the latest tables of atomic weights[1] contain many values computed from physical measurements.

Recently, HUIZENGA and WAPSTRA,[2] using mass-spectroscopic and nuclear-reaction data, prepared a table of isotopic masses. This paper describes a table of atomic weights of elements computed from these data. The isotopic masses are given in the physical scale of atomic weights. They are converted to the chemical scale with help of the conversion factor given by NIER[3]

$$M_{\text{chem}}/M_{\text{phys}} = 1{\cdot}000{,}278{,}3 \pm 0{\cdot}000{,}000{,}5$$

Table 1 presents the isotopic constitutions adopted in this computation. The values are averages of results obtained by different workers; references are generally made only to the last published paper for each element. The data are rounded off to multiples of 0·05% if the available information does not warrant higher precision. Most data in Table 1 agree with the values adopted by BAINBRIDGE and NIER;[4] in cases where new information has become available, some deviations may occur.

Table 2 presents the computed atomic weights and, for comparison, the values adopted in WICHERS[1] last report. The quoted errors for elements containing only one isotope are mainly due to the uncertainties in the isotopic masses; those for complex elements are essentially caused by the errors in the isotopic constitutions.

We thank Prof. Dr. A. H. W. ATEN and Prof. Dr. P. C. GUGELOT for their interest. This work is part of a program of the Foundation for Fundamental Research of Matter (FOM) of the Organization for Pure Scientific Research (ZWO).

[1] E. WICHERS *J. Amer. Chem. Soc.* **74**, 2447 (1952); **76**, 2033 (1954).
[2] A. H. WAPSTRA *Physica* **21**, 367 and 385 (1955); J. R. HUIZENGA *Physica* **21**, 410 (1956).
[3] A. O. NIER *Phys. Rev.* **77**, 789 (1950).
[4] R. T. BAINBRIDGE and A. O. NIER *Preliminary report no.* 9, National Research Council (1950).



1

TABLE 1.—PERCENTAGE NATURAL ABUNDANCES OF ISOTOPES

| Element | A | % | Element | A | % | Element | A | % |
|---|---|---|---|---|---|---|---|---|
| H[1] | 1 | 99·985 | Cr | 53 | 9·55 | Mo | 95 | 15·70 |
| | 2 | 0·015 | | 54 | 2·38 | | 96 | 16·50 |
| He[21] | 3 | 0·00013 | Mn | 55 | 100 | | 97 | 9·45 |
| | 4 | 99·99987 | Fe[9,19] | 54 | 5·84 | | 98 | 23·75 |
| Li[40] | 6 | 7·98 | | 56 | 91·65 | | 100 | 9·65 |
| | 7 | 92·02 | | 57 | 2·19 | Ru[26] | 96 | 5·55 |
| Be | 9 | 100 | | 58 | 0·32 | | 98 | 2·00 |
| B[16, 20] | 10 | 18·85 | Co | 59 | 100 | | 99 | 12·75 |
| | 11 | 81·15 | Ni[25] | 58 | 67·85 | | 100 | 12·70 |
| | 12 | 98·885 | | 60 | 26·20 | | 101 | 17·00 |
| | 13 | 1·115 | | 61 | 1·20 | | 102 | 31·45 |
| N[21] | 14 | 99·636 | | 62 | 3·65 | | 104 | 18·55 |
| | 15 | 0·364 | | 64 | 1·10 | Rh | 103 | 100 |
| O[21] | 16 | 99·7587 | Cu[19,20] | 63 | 69·1 | Pd[29] | 102 | 0·96 |
| | 17 | 0·0374 | | 65 | 30·9 | | 104 | 10·97 |
| | 18 | 0·2039 | Zn[20] | 64 | 48·90 | | 105 | 22·23 |
| F | 19 | 100 | | 66 | 27·81 | | 106 | 27·32 |
| Ne[32] | 20 | 90·92 | | 67 | 4·12 | | 108 | 26·71 |
| | 21 | 0·257 | | 68 | 18·55 | | 110 | 11·81 |
| | 22 | 8·823 | | 70 | 0·62 | Ag[10] | 107 | 51·35 |
| Na | 23 | 100 | Ga[17] | 69 | 60·1 | | 109 | 48·65 |
| Mg[19] | 24 | 78·60 | | 71 | 39·9 | Cd[15, 19] | 106 | 1·22 |
| | 25 | 10·11 | Ge[27] | 70 | 20·60 | | 108 | 0·91 |
| | 26 | 11·29 | | 72 | 27·43 | | 110 | 12·37 |
| Al | 27 | 100 | | 73 | 7·84 | | 111 | 12·76 |
| Si[37] | 28 | 92·17 | | 74 | 36·40 | | 112 | 24·04 |
| | 29 | 4·71 | | 76 | 7·73 | | 113 | 12·28 |
| | 30 | 3·12 | As | 75 | 100 | | 114 | 28·82 |
| P | 31 | 100 | Se[19] | 74 | 0·87 | | 116 | 7·60 |
| S[32] | 32 | 95·018 | | 76 | 9·02 | In[19] | 113 | 4·23 |
| | 33 | 0·750 | | 77 | 7·58 | | 115 | 95·77 |
| | 34 | 4·215 | | 78 | 23·52 | Sn[14,19] | 112 | 0·95 |
| | 36 | 0·017 | | 80 | 49·82 | | 114 | 0·65 |
| Cl[2] | 35 | 75·4 | | 82 | 9·19 | | 115 | 0·34 |
| | 37 | 24·6 | Br[19, 43] | 79 | 50·51 | | 116 | 14·24 |
| A[21] | 36 | 0·337 | | 81 | 49·49 | | 117 | 7·57 |
| | 38 | 0·063 | Kr[33] | 78 | 0·35 | | 118 | 24·01 |
| | 40 | 99·600 | | 80 | 2·27 | | 119 | 8·58 |
| K[21, 24] | 39 | 99·08 | | 82 | 11·56 | | 120 | 32·97 |
| | 40 | 0·012 | | 83 | 11·51 | | 122 | 4·71 |
| | 41 | 6·908 | | 84 | 56·94 | | 124 | 5·98 |
| Ca[19] | 40 | 96·92 | | 86 | 17·37 | Sb[19] | 121 | 57·25 |
| | 42 | 0·64 | Rb[33] | 85 | 72·15 | | 123 | 42·75 |
| | 43 | 0·13 | | 87 | 27·85 | Te[19] | 120 | 0·09 |
| | 44 | 2·13 | Sr[19] | 84 | 0·55 | | 122 | 2·46 |
| | 46 | 0·003 | | 86 | 9·80 | | 123 | 0·87 |
| | 48 | 0·177 | | 87 | 7·00 | | 124 | 4·61 |
| Sc | 45 | 100 | | 88 | 82·65 | | 125 | 6·99 |
| Ti[11] | 46 | 7·99 | Y | 89 | 100 | | 126 | 18·71 |
| | 47 | 7·32 | Zr[19] | 90 | 51·46 | | 128 | 31·78 |
| | 48 | 73·98 | | 91 | 11·23 | | 130 | 34·49 |
| | 49 | 5·46 | | 92 | 17·11 | I | 127 | 100 |
| | 50 | 5·25 | | 94 | 17·40 | Xe[33] | 124 | 0·095 |
| V[35, 35] | 50 | 0·24 | | 96 | 2·80 | | 126 | 0·089 |
| | 51 | 99·76 | Nb | 93 | 100 | | 128 | 1·918 |
| Cr[19] | 50 | 4·31 | Mo[7] | 92 | 15·85 | | 129 | 26·34 |
| | 52 | 83·76 | | 94 | 9·10 | | 130 | 4·068 |

TABLE 1 (*continued*)

| Element | *A* | % | Element | *A* | % | Element | *A* | % |
|---|---|---|---|---|---|---|---|---|
| Xe | 131 | 21·21 | Gd | 157 | 15·65 | W | 183 | 14·30 |
| | 132 | 26·91 | | 158 | 24·90 | | 184 | 30·67 |
| | 134 | 10·48 | | 160 | 21·90 | | 186 | 28·70 |
| | 136 | 8·89 | Tb | 159 | 100 | Re[19] | 185 | 37·07 |
| Cs | 133 | 100 | Dy[26] | 156 | 0·055 | | 187 | 62·93 |
| Ba[5] | 130 | 0·102 | | 158 | 0·095 | Os[4] | 184 | 0·02 |
| | 132 | 0·098 | | 160 | 2·30 | | 186 | 1·59 |
| | 134 | 2·42 | | 161 | 18·85 | | 187 | 1·64 |
| | 135 | 6·59 | | 162 | 25·45 | | 188 | 13·25 |
| | 136 | 7·81 | | 163 | 24·95 | | 189 | 16·15 |
| | 137 | 11·32 | | 164 | 28·30 | | 190 | 26·40 |
| | 138 | 71·66 | Ho | 165 | 100 | | 192 | 40·95 |
| La[11] | 138 | 0·089 | Er[27,28] | 162 | 0·14 | Ir[3] | 191 | 38·5 |
| | 139 | 99·911 | | 164 | 1·56 | | 193 | 61·5 |
| Ce[11] | 136 | 0·19 | | 166 | 33·40 | Pt[30,32,33] | 190 | 0·01 |
| | 138 | 0·25 | | 167 | 22·90 | | 192 | 0·78 |
| | 140 | 88·49 | | 168 | 27·05 | | 194 | 32·8 |
| | 142 | 11·07 | | 170 | 14·95 | | 195 | 33·8 |
| Pr | 141 | 100 | Tm | 169 | 100 | | 196 | 25·4 |
| Nd[36] | 142 | 27·09 | Yb[29] | 168 | 0·14 | | 198 | 7·21 |
| | 143 | 12·14 | | 170 | 3·03 | Au | 197 | 100 |
| | 144 | 23·85 | | 171 | 14·30 | Hg[9,33] | 196 | 0·15 |
| | 145 | 8·29 | | 172 | 21·80 | | 198 | 10·05 |
| | 146 | 17·26 | | 173 | 16·13 | | 199 | 16·95 |
| | 148 | 5·74 | | 174 | 31·85 | | 200 | 23·15 |
| | 150 | 5·63 | | 176 | 12·75 | | 201 | 13·20 |
| Sm[12,13] | 144 | 3·10 | Cp[27] | 175 | 97·40 | | 202 | 29·75 |
| | 147 | 15·00 | | 176 | 2·60 | | 204 | 6·75 |
| | 148 | 11·20 | Hf[37] | 174 | 0·19 | Tl[19] | 203 | 29·50 |
| | 149 | 13·80 | | 176 | 5·20 | | 205 | 70·50 |
| | 150 | 7·40 | | 177 | 18·46 | Pb[10] | 204 | 1·5 |
| | 152 | 26·80 | | 178 | 27·10 | | 206 | 23·6 |
| | 154 | 22·70 | | 179 | 13·75 | | 207 | 22·6 |
| Eu[10] | 151 | 47·77 | | 180 | 35·30 | | 208 | 52·3 |
| | 153 | 52·23 | Ta[42] | 180 | 0·012 | Bi | 209 | 100 |
| Gd[20] | 152 | 0·20 | | 181 | 99·988 | U[6,26] | 234 | 0·006 |
| | 154 | 2·15 | W[17,23] | 180 | 0·13 | | 235 | 0·714 |
| | 155 | 14·75 | | 182 | 26·20 | | 238 | 99·280 |
| | 156 | 20·45 | | | | | | |

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(1) HALL and JONES *J. Amer. Chem. Soc.* **58**, 1915 (1936).
(2) NIER and HANSON *Phys. Rev.* **50**, 722 (1936).
(3) SAMPSON and BLEAKNEY *Phys. Rev.* **50**, 732 (1936).
(4) NIER *Phys. Rev.* **52**, 885 (1937).
(5) NIER *Phys. Rev.* **54**, 275 (1938).
(6) NIER *Phys. Rev.* **55**, 150 (1939).
(7) WILLIAMS and YUSTER *Phys. Rev.* **69**, 556 (1946).
(8) INGHRAM *et al. Phys. Rev.* **71**, 561 (1947).
(9) VALLEY and ANDERSON *J. Amer. Chem. Soc.* **69**, 1871 (1947).
(10) INGHRAM *et al.* ANL 4012, 7 (1947).
(11) INGHRAM *et al. Phys. Rev.* **72**, 967 (1947).
(12) INGHRAM *et al. Phys. Rev.* **73**, 180 (1948).
(13) MATTAUCH and SCHELDT *Z. Naturforsch.* **3**, 105 (1948).
(14) HINTENBERGER *et al. Z. Naturforsch.* **3**, 413 (1948).
(15) LELAND and NIER *Phys. Rev.* **73**, 1206 (1948).
(16) THODE *et al. J. Amer. Chem. Soc.* **70**, 3008 (1948).
(17) INGHRAM *et al. Phys. Rev.* **74**, 343 (1948).
(18) HESS *Phys. Rev.* **74**, 773 (1948).
(19) WHITE and CAMERON *Phys. Rev.* **74**, 991 (1948).
(20) HESS *et al. Phys. Rev.* **74**, 1531 (1948).
(21) COON *Phys. Rev.* **75**, 1355 (1949).
(22) DUCKWORTH *et al. Phys. Rev.* **75**, 1438 (1949).
(23) LELAND *Phys. Rev.* **76**, 992 (1949).
(24) HESS and INGHRAM *Phys. Rev.* **76**, 1717 (1949).
(25) LELAND *Phys. Rev.* **76**, 1722 (1949).
(26) HIBBS Y-604 (1949).
(27) HAYDEN *et al. Phys. Rev.* **77**, 299 (1950).
(28) LELAND *Phys. Rev.* **77**, 634 (1950).
(29) BECKER and VOGEL *Z. Naturforsch.* **5a**, 174 (1950).
(30) OSBERGHAUS *Z. Physik* **128**, 366 (1950).
(31) NIER *Phys. Rev.* **77**, 789 (1950).
(32) MACNAMARA and THODE *Phys. Rev.* **78**, 307 (1950).
(33) NIER *Phys. Rev.* **79**, 450 (1950).
(34) REUTERSÄRD *Ark. f. Fys.* **4**, 203 (1952).
(35) MATTRAW and PACHUCKI *Nucl. Sci. Abstract* **6**, 2526 (1952).
(36) WALKER and THODE *Phys. Rev.* **90**, 447 (1953).
(37) REYNOLDS *Phys. Rev.* **90**, 1047 (1953).
(38) FRIEDMAN and IRSA *J. Amer. Chem. Soc.* **75**, 5741 (1953).
(39) SITES *Phys. Rev.* **92**, 1096 A (1953).
(40) HUTCHINSON *Phys. Rev.* **96**, 1018 (1954).
(41) HOGG *Canad. J. Chem.* **32**, 1039 (1954).
(42) WHITE *et al. Phys. Rev.* **97**, 566 (1955).
(43) CAMERON and SIPPERT *Science* **121**, 136 (1955).

TABLE 2.—ATOMIC WEIGHTS COMPUTED FROM PHYSICAL MEASUREMENTS

| Element | Z | Atomic weight | *J. Amer. Chem. Soc.* **76**, 2033 | Element | Z | Atomic weight | *J. Amer Chem. Soc.* **76**, 2033 |
|---|---|---|---|---|---|---|---|
| A | 18 | 39·94920 ± 0·00007 | 39·944 | Mo | 42 | 95·892 ± 0·005 | 95·95 |
| Ac | 89 | 227·036 ± 0·002 | | N | 7 | 14·00725 ± 0·00002 | 14·008 |
| Ag | 47 | 107·8821 ± 0·0014 | 107·880 | Na | 11 | 22·99065 ± 0·00002 | 22·991 |
| Al | 13 | 26·98257 ± 0·00002 | 26·98 | Nb | 41 | 92·9094 ± 0·0003 | 92·91 |
| As | 33 | 74·92455 ± 0·00010 | 74·91 | Nd | 60 | 144·248 ± 0·003 | 144·27 |
| Au | 79 | 196·974 ± 0·003 | 197·0 | Ne | 10 | 20·1722 ± 0·0008 | 20·183 |
| B | 5 | 10·822 ± 0·002 | 10·82 | Ni | 28 | 58·708 ± 0·015 | 58·69 |
| Ba | 56 | 137·332 ± 0·005 | 137·36 | O | 8 | 16·— | 16·— |
| Be | 4 | 9·01254 ± 0·00001 | 9·013 | Os | 76 | 190·244 ± 0·008 | 190·2 |
| Bi | 83 | 208·988 ± 0·002 | 209·00 | P | 15 | 30·97494 ± 0·00003 | 30·975 |
| Br | 35 | 79·9103 ± 0·0015 | 79·916 | Pa | 91 | 231·044 ± 0·002 | |
| C | 6 | 12·01165 ± 0·00003 | 12·011 | Pb | 82 | 207·225 ± 0·015 | 207·21 |
| Ca | 20 | 40·080 ± 0·002 | 40·08 | Pd | 46 | 106·434 ± 0·002 | 106·7 |
| Cb | | see Nb | | Po | 84 | 209·990 ± 0·002 | |
| Cd | 48 | 112·427 ± 0·003 | 112·41 | Pr | 59 | 140·9119 ± 0·0010 | 140·92 |
| Ce | 58 | 140·119 ± 0·005 | 140·13 | Pt | 78 | 195·090 ± 0·008 | 195·23 |
| Cl | 17 | 35·461 ± 0·004 | 35·457 | Ra | 88 | 226·033 ± 0·002 | 226·05 |
| Co | 27 | 58·9355 ± 0·0003 | 58·94 | Rb | 37 | 85·4715 ± 0·0006 | 85·48 |
| Cp | 71 | 174·973 ± 0·004 | 174·99 | Re | 75 | 186·217 ± 0·003 | 186·31 |
| Cr | 24 | 51·9996 ± 0·0015 | 52·01 | Rh | 45 | 102·9093 ± 0·0005 | 102·91 |
| Cs | 55 | 132·9102 ± 0·0007 | 132·91 | Ru | 44 | 101·061 ± 0·010 | 101·1 |
| Cu | 29 | 63·5494 ± 0·0015 | 63·54 | S | 16 | 32·0656 ± 0·0003 | 32·066 |
| Dy | 66 | 162·508 ± 0·010 | 162·46 | Sb | 51 | 121·764 ± 0·002 | 121·76 |
| Er | 68 | 167·269 ± 0·007 | 167·2 | Sc | 21 | 44·95756 ± 0·00012 | 44·96 |
| Eu | 63 | 151·971 ± 0·005 | 152·0 | Se | 34 | 78·993 ± 0·006 | 78·96 |
| F | 9 | 18·99916 ± 0·00002 | 19·00 | Si | 14 | 28·0874 ± 0·0010 | 28·09 |
| Fe | 26 | 55·8488 ± 0·0008 | 55·85 | Sm | 62 | 150·391 ± 0·020 | 150·43 |
| Ga | 31 | 69·726 ± 0·004 | 69·72 | Sn | 50 | 118·752 ± 0·008 | 118·70 |
| Gd | 64 | 157·262 ± 0·010 | 156·9 | Sr | 38 | 87·6219 ± 0·0010 | 87·63 |
| Ge | 32 | 72·629 ± 0·005 | 72·60 | Ta | 73 | 180·952 ± 0·002 | 180·95 |
| H | 1 | 1·00802 ± 0·00001 | 1·008 | Tb | 65 | 158·933 ± 0·004 | 158·93 |
| He | 2 | 4·00276 ± 0·00001 | 4·003 | Te | 52 | 127·633 ± 0·006 | 127·61 |
| Hf | 72 | 178·493 ± 0·005 | 178·6 | Th | 90 | 232·046 ± 0·002 | 232·05 |
| Hg | 80 | 200·597 ± 0·005 | 200·61 | Ti | 22 | 47·877 ± 0·004 | 47·90 |
| Ho | 67 | 164·935 ± 0·002 | 164·94 | Tl | 81 | 204·391 ± 0·002 | 204·39 |
| I | 53 | 126·9095 ± 0·0005 | 126·91 | Tm | 69 | 168·940 ± 0·004 | 168·94 |
| In | 49 | 114·8231 ± 0·0008 | 114·76 | U | 92 | 238·037 ± 0·002 | 238·07 |
| Ir | 77 | 192·200 ± 0·005 | 192·2 | V | 23 | 50·94346 ± 0·00015 | 50·95 |
| K | 19 | 39·1034 ± 0·0008 | 39·100 | W | 74 | 183·857 ± 0·010 | 183·92 |
| Kr | 36 | 83·804 ± 0·002 | 83·80 | Xe | 54 | 131·314 ± 0·003 | 131·3 |
| La | 57 | 138·9099 ± 0·0010 | 138·92 | Y | 39 | 88·9093 ± 0·0002 | 88·92 |
| Li | 3 | 6·9368 ± 0·0018 | 6·940 | Yb | 70 | 173·044 ± 0·007 | 173·04 |
| Lu | | see Cp | | Zn | 30 | 65·389 ± 0·003 | 65·38 |
| Mg | 12 | 24·3127 ± 0·0017 | 24·32 | Zr | 40 | 91·227 ± 0·005 | 91·22 |
| Mn | 25 | 54·9401 ± 0·0002 | 54·94 | | | | |

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 333 to 344. Pergamon Press Ltd., London

# ALPHA-DECAY HINDRANCE-FACTOR CALCULATIONS

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**Abstract**—The hindrance factor, $F$, in alpha decay is defined in terms of constants $A$ and $B$ which are empirically determined for each element. The determination of $A$ and $B$ by fitting even-even alpha-decay rates is discussed. Using these values, hindrance factors for all known alpha groups of alpha emitters with greater than 128 neutrons and 83 protons have been calculated. The results are divided into four groups corresponding to odd-odd, odd-even, even-odd, and excited states of even-even alpha emitters. Hindrance factor distributions are presented in histogram form.

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## 1. INTRODUCTION

THEORETICAL expressions relating alpha-decay rate and energy by a barrier penetration treatment were first derived by GAMOW[1] and GURNEY and CONDON.[2] The relationships hold best for even-even alpha emitters. PERLMAN, SEABORG, and GHIORSO[3] in their alpha systematics have pointed out large and erratic hindrance in odd types. NORDSTROM[4] has plotted distributions of hindrance factors in an attempt to classify "forbiddenness" in alpha decay in a manner similar to classification of log $ft$ values in beta decay. We have made hindrance-factor plots for all observed alpha groups emitted from nuclei with greater than 128 neutrons in an attempt to establish correlations.

Decay rates to ground states of even-even nuclei are correlated remarkably well by simple barrier penetration formulas with smoothly varying radius formulas. However, there are significant radius deviations shown by plotting[5] the "effective nuclear radii" for even-even alpha emitters. For semi-empirical correlations of alpha-decay rates it would be desirable to plot decay-rate data of even-even nuclei in a manner that would give nearly straight lines for isotopes of a given element. Such a plot is suggested by barrier penetration theory, as we shall show later in this paper. In this plot one sets the logarithm of the half-life against the reciprocal of the square root of the total effective alpha-decay energy $Q_{\text{eff}}$. $Q_{\text{eff}}$ equals alpha-particle energy $E$ plus recoil energy $\frac{M_\alpha E}{M_r}$ plus $\Delta E_{\text{sc}}$, the orbital electron "screening" correction. $\Delta E_{\text{sc}}$ can be obtained from the relationship:

$$\Delta E_{\text{sc}} = 65{\cdot}3\,(Z+2)^{7/5} - 80\,(Z+2)^{2/5}\ ev, \tag{1}$$

where $Z$ is the atomic number of the daughter nucleus.

### DEFINITIONS OF HINDRANCE FACTOR

The hindrance-factor (or departure-factor) concept has been employed for several years in alpha-decay rate discussions. By general usage it is that factor by which

[1] G. GAMOW *Z. Physik* **51**, 204 (1928); G. GAMOW and C. L. CRITCHFIELD *Theory of Atomic Nucleus and Nuclear Energy Sources* Clarendon Press, Oxford, Chapter VI (1949).
[2] E. U. CONDON and R. W. GURNEY *Phys. Rev.* **33**, 127 (1929); *Nature* **122**, 439 (1928).
[3] I. PERLMAN, G. T. SEABORG, and A. GHIORSO *Phys. Rev.* **77**, 26 (1950).
[4] S. G. NORDSTRÖM Note on the Departure Factor in α-Decay MANNE SIEGBAHN p. 587 Almquist and Wiksells Bokryckeri AB, Uppsala (1951).
[5] I. PERLMAN and F. ASARO *Ann. Rev. Nuclear Sci.* **4**, (1954); F. S. STEPHENS JR., private communication.

a given alpha-decay transition is slower than would be expected from systematics based on ground-state transition rates of the nearest even-even neighbours. There has been need for more precise mathematical definition of hindrance factors and for simple analytical expressions by which to calculate them, once defined. At the risk of some arbitrariness and the admitted inapplicability of the definitions for the isotopes of less than 128 neutrons, we should like to establish a basis for hindrance-factor calculations by the following procedure which is consistent with earlier definitions:

The decay-rate data for ground-state groups of even-even isotopes for each even $Z$ element should be separately used to determine by least-squares fitting the best values for constants $A_Z$ and $B_Z$ in the expression

$$\log_{10} t_{1/2\alpha} = A_Z Q_{\text{eff}}^{-1/2} + B_Z \tag{2}$$

where $t_{1/2\alpha}$ is the partial ground-state alpha half-life in seconds, and $Q_{\text{eff}}$ is the effective total decay energy in MeV.

(a) The hindrance factor, $F$, for an alpha group of an even-odd nucleus is obtained by substituting that group's partial half-life and $Q_{\text{eff}}$ into the expression

$$\log_{10} F = \log_{10} t_{1/2\alpha} - A_Z Q_{\text{eff}}^{-1/2} - B_Z \tag{3}$$

with $A_Z$ and $B_Z$ for that particular element being used.

(b) The hindrance factors for odd-even and odd-odd alpha-emitter groups are to be calculated from (3) by using for $A_Z$ and $B_Z$ the arithmetical mean of the corresponding values for the two adjacent even atomic numbers.

(c) The hindrance factors to excited states of an even-even nucleus are given a special definition to make the basis of comparison its own ground-state transition. That is, the hindrance factor $F_e$ for even-even nuclei is equal to the $F$ value calculated from (3) in the usual manner for the excited-state group divided by the $F$ value similarly calculated for the ground-state group.

## NUMERICAL APPLICATION

The constants $A$ and $B$ that we determined by least-squares analyses of even-even data are listed in Table 1. The slope for fermium was obtained by extrapolation of a least-square fit of line slopes for all even $Z$. The fermium intercept was obtained in a similar manner. The solid lines in Fig. 1 are those defined by the constants in Table 1.

The data used to fit the lines include only isotopes with accurately known energy

TABLE 1.—SEMI-EMPIRICAL CONSTANTS* FROM CORRELATION OF GROUND STATE DECAY RATES OF EVEN-EVEN NUCLEI

| Element | $A$ | $B$ |
|---|---|---|
| 100 Fm | 156·38† | −53·3742† |
| 98 Cf | 152·86 | −52·9506 |
| 96 Cm | 152·44 | −53·6825 |
| 94 Pu | 146·23 | −52·0899 |
| 92 U | 147·49 | −53·6565 |
| 90 Th | 144·19 | −53·2644 |
| 88 Ra | 139·17 | −52·1476 |
| 86 Em | 137·46 | −52·4597 |
| 84 Po | 129·35 | −49·9229 |

* Constants to use with equation (3), where $t_{1/2\alpha}$ is in seconds and $Q_{\text{eff}}$ in MeV.
† Values resulting from extrapolation.

and half-life. We decided to use only isotopes whose decay energies were determined by the use of a magnetic spectrograph. We examined the data from which the partial alpha half-life is calculated and concluded that it was sufficiently good for all isotopes with spectrographically determined energies. The isotopes used in fitting the curve are shown by solid triangles in Fig. 1. Solid circles indicate even-even isotopes not used in the least-squares analyses. $Po^{212}$ and $Em^{218}$ were not used despite precise energy and

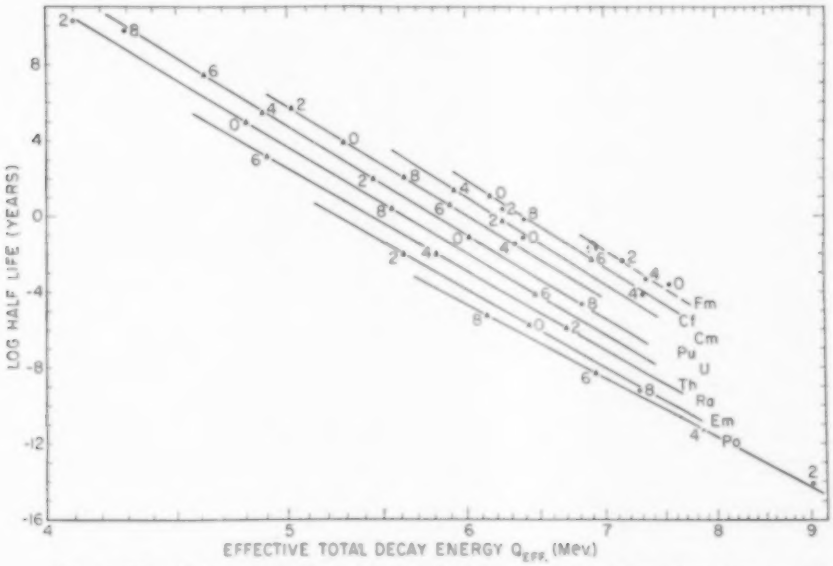


FIG. 1.—Plot of logarithms of partial alpha half-lives for ground-state transitions vs. the inverse square root of the effective total alpha-decay energy. The solid lines represent least-squares fits to data represented by solid triangles, for $Z$ between 84 and 98. These least-squares fits were used to calculate hindrance factors. Constants in the equations for these lines are given in Table I. Solid circles represent data not used in the least-squares analyses. The last digit in the mass number of the alpha emitter is given beside each point.

half-life knowledge because they deviate markedly from systematic behaviour. $Cf^{252}$ and $Fm^{254}$ were not used because they lie beyond the 152-neutron subshell.[6]

All alpha-particle data used throughout this paper were taken from the compilation of F. ASARO[7] with the exception of the recent data for $Pu^{233}$ [8] and $Pu^{237}$.[9]

## THEORETICAL CONSIDERATIONS

It is easy to justify the above-mentioned type of plot from WKB barrier penetration formulas (the form for $S$-wave emission). The most important factor in these formulas is the exponential expression

$$P = \exp\left[-\frac{2}{\hbar}\int_R^{\frac{2Ze^2}{Q}}\left[2M\left(\frac{2Ze^2}{r}-Q\right)\right]^{1/2}dr\right] \tag{4}$$

[6] A. GHIORSO, S. G. THOMPSON, G. H. HIGGINS, B. G. HARVEY, and G. T. SEABORG *Phys. Rev.* **95**, 293 (1954).
[7] I. PERLMAN and J. O. RASMUSSEN Alpha Radioactivity, Vol. 42, *Handbuch der Physik* Springer-Verlag, Berlin (to be published).
[8] T. D. THOMAS and R. A. GLASS, private communication (1956).
[9] R. VANDENBOSCH and R. A. GLASS, private communication (1956).

which is expressible in analytical form as

$$\exp\left[-\frac{2}{\hbar}(2MB)^{1/2}R\right]\left[x^{-1/2}\arccos x^{1/2}-(1-x)^{1/2}\right] \tag{5}$$

where $x = QR/2Ze^2$, a dimensionless parameter, and $B = 2Ze^2/R$, the barrier height.

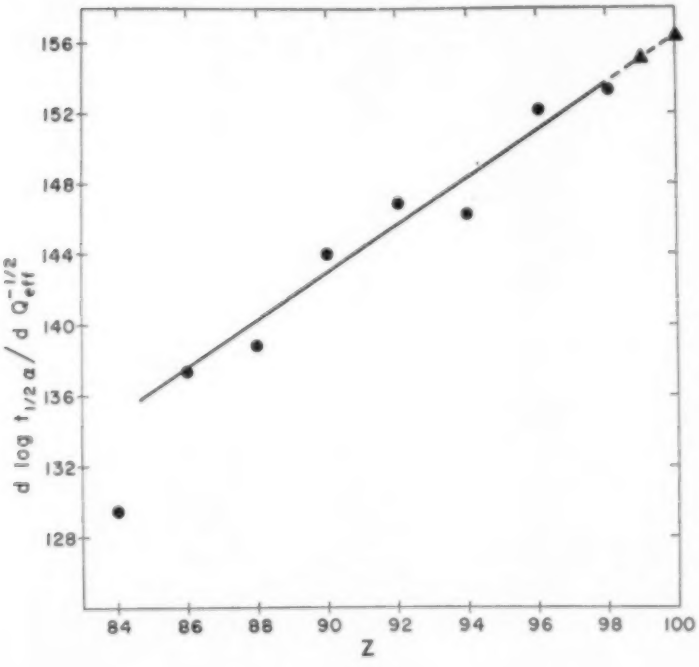


FIG. 2.—Plot of $\frac{d \log t_{\frac{1}{2}\alpha}}{dQ_{\mathrm{eff}}{}^{-\frac{1}{2}}}$ as a function of $Z$.

The dotted line indicates the method used to obtain slopes for elements 99 and 100.

If we make a Taylor-series expansion of this function about $x = 0$, we obtain

$$P \approx \exp\left\{-\frac{(2M)^{1/2}B^{1/2}R}{\hbar}\left[\frac{\pi B^{1/2}}{Q^{1/2}}-4+\frac{Q}{B}-\frac{3}{4}\frac{Q^2}{B^2}+\ldots\right]\right\} \tag{6}$$

If one retains only the dominant first two terms, then one sees that the logarithm of the penetration function is a linear function of $Q^{-1/2}$.

An interesting check on simple barrier-penetration theory is provided by examination of the slopes of the least-squares lines of Fig. 1. The form of the first term of equation (6) shows that the slopes of the lines of Fig. 1 should be proportional to the atomic number, $Z$, of the daughter nucleus to accord with simple theory. In Fig. 2 these slopes are plotted against $Z$. The theoretically expected behaviour is well shown, although some deviations occur.

It is beyond the scope of this paper to attempt any detailed theoretical explanation

of the deviations from simple theory. It should be pointed out that abnormal slopes in Fig. 1 do not necessarily mean a changed dependence of decay rate on energy, but since energy is (above 128 neutrons) a monotonic function of the neutron number for an isotopic series, an abnormal slope may reflect a change in the alpha-decay rate dependent on the addition of neutron pairs. Some isotopic series pass through the region of the onset of validity of the Bohr-Mottelson[10] spheroidally deformed model and some pass through rapidly changing spheroidal deformation. Such changes must certainly influence barrier penetration, yet with the exception of polonium, which is only two protons removed from the closed proton shell at 82, the behaviour of the slopes is relatively constant. (The slopes should also be influenced by variations in the alpha formation probability entirely apart from the external barrier penetration factor.)

## EVEN-EVEN NUCLEI—EXCITED-STATE TRANSITIONS

In contrast to the regularly behaving ground-state transition rates, the transitions to excited states show striking trends in rate for different nuclei.

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For the elements thorium and above, alpha decay has frequently been observed to at least three levels (0+, 2+, and 4+), identifiable as a rotational band sequence. Alpha decay to states of odd parity has also been observed.[5]

To exhibit this behaviour, we have calculated hindrance factors to all observed states. The distributions of hindrance factors are shown in the histograms of Figs. 3, 4, 5, 6, and 7. The three lines of numbers on each histogram block represent (1) element/mass number, (2) energy of excited state in keV, and (3) the value of the hindrance factor, $F_e$, for this transition. Because of the increasing interest in the correlations achieved by the Bohr-Mottelson large-deformation model, we have segregated the cases in the region of nuclear rotational bands from those cases nearer the $Pb^{208}$ closed configuration. Somewhat arbitrarily we have made the division at 138 neutrons. The bold line on each histogram divides these regions, the cases below the bold line coming from the rotational band region above 138 neutrons.

For the even-even nuclides the generally increasing nature of hindrance to the higher groups is evident, and the hindrance to the 4+, 6+, and 8+ groups generally far exceeds hindrance attributable to the addition to the barrier of the centrifugal potential associated with angular momentum of the alpha-decay system.

ASARO[11] has plotted hindrance factors against atomic number for excited-state transitions. In similar manner we have plotted hindrance factors against neutron number in Fig. 8.

The dependence upon neutron number of decay to the first excited state (2+) is slight, the groups being at lower mass relatively unhindered but showing some increase among the heaviest nuclei studied.

Striking variation is seen in the dependence of decay to the second excited state (4+) upon $N$ and $Z$. It can easily be seen from Fig. 8 that the hindrance factors for the second state vary with $Z$ and pass through a maximum at $Z = 96$. However, also notable is the apparent neutron dependence of isotopes, as manifested by the apparent maxima in the 4+ curves of thorium and uranium. Recent experimental evidence[12] indicates that the hindrance factors for the 1— states also pass through a maximum and drop at $Cm^{242}$.

[10] A. BOHR and B. R. MOTTELSON *Kgl. Danske Vid Selskab, Mat.-fys. Medd.* **27**, No. 16 (1953).
[11] F. S. STEPHENS JR., Ph.D. Thesis, University of California, 1955 (UCRL-2970) (unpublished).
[12] F. ASARO and F. S. STEPHENS JR., private communication (1956).

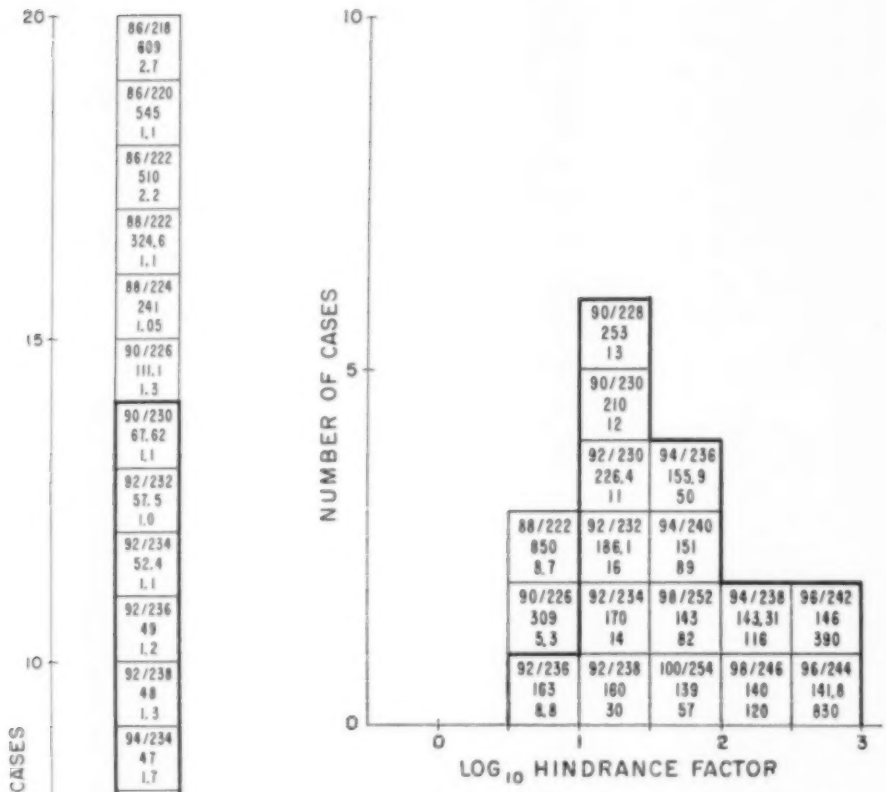


FIG. 4.—Distribution of hindrance factors for alpha decay to 4+ states in even-even nuclei.

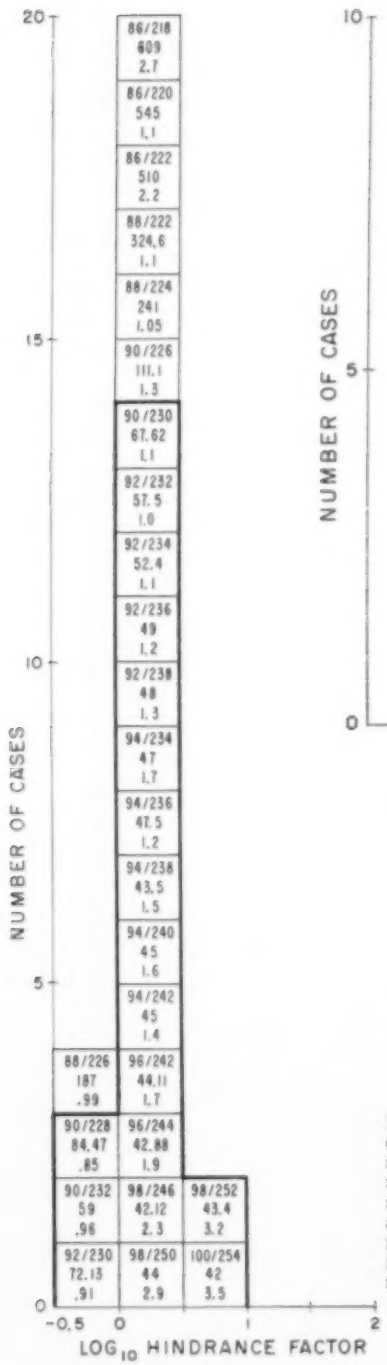


FIG. 3.—Distribution of hindrance factors for alpha decay to 2+ states in even-even nuclei. Heavy line in all histograms separates rotational region from region nearer closed shells, where rotational model is not applicable. First line of numbers indicates element and mass assignment; second, best experimental value for energy of state; third, value of the hindrance factor for alpha decay to this state. These designations apply to the histograms for the 4+, 6+, 8+, and 1− states also.

The relative intensities of decay groups to the even parity states have been considered by a number of authors in connection with the theory of alpha decay of spheroidal nuclei,[13] but these interpretations will not be discussed here.

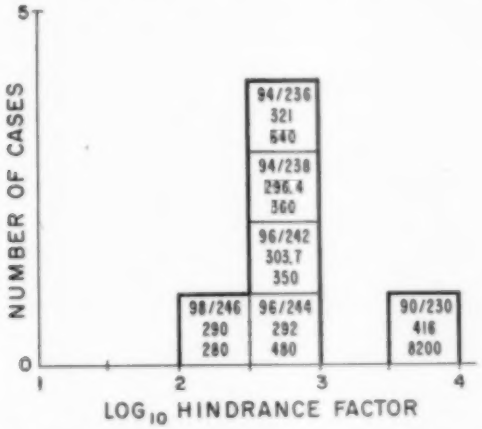


FIG. 5.—Distribution of hindrance factors for alpha decay to 6+ states in even-even nuclei.

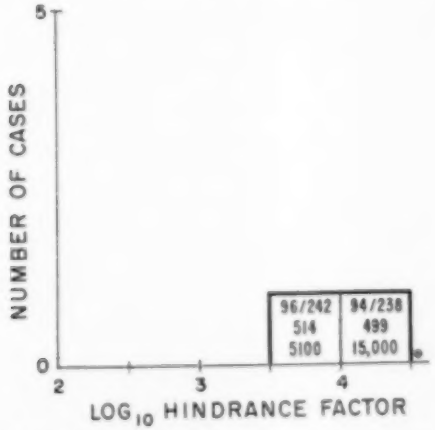


FIG. 6.—Distribution of hindrance factors for alpha decay to 8+ states in even-even nuclei.

## ODD-NUCLEON ALPHA EMITTERS

In contrast to the regular behaviour of even-even alpha-decay rates, nuclei with odd nucleon numbers often exhibit erratic alpha-decay rates, tending generally to be slower than comparable even-even alpha emitters. PERLMAN, GHIORSO, and SEABORG[3] have clearly pointed out that the hindrance must be associated with a lowered alpha-formation probability rather than with the higher external barrier resulting from non-zero angular momentum. The details regarding this hindrance are not well

[13] J. O. RASMUSSEN, University of California Radiation Laboratory Unclassified Report UCRL-2431 (1953); R. F. CHRISTY *Phys. Rev.* **98**, ZA7, 1205 (1955); J. O. RASMUSSEN and B. SEGALL, University of California Radiation Laboratory Unclassified Report UCRL-3040 (1955) *Phys. Rev.* (in press).

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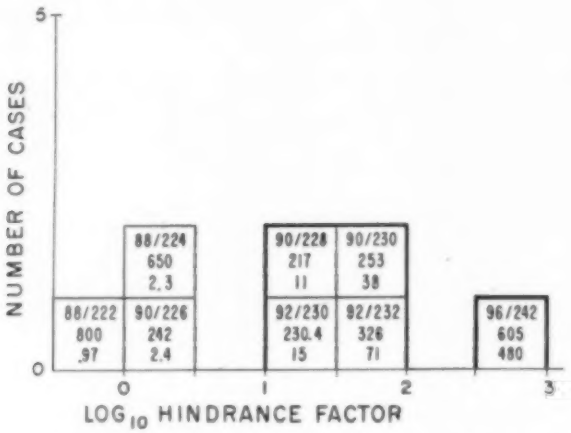


FIG. 7.—Distribution of hindrance factors for alpha decay to 1− states in even-even nuclei.

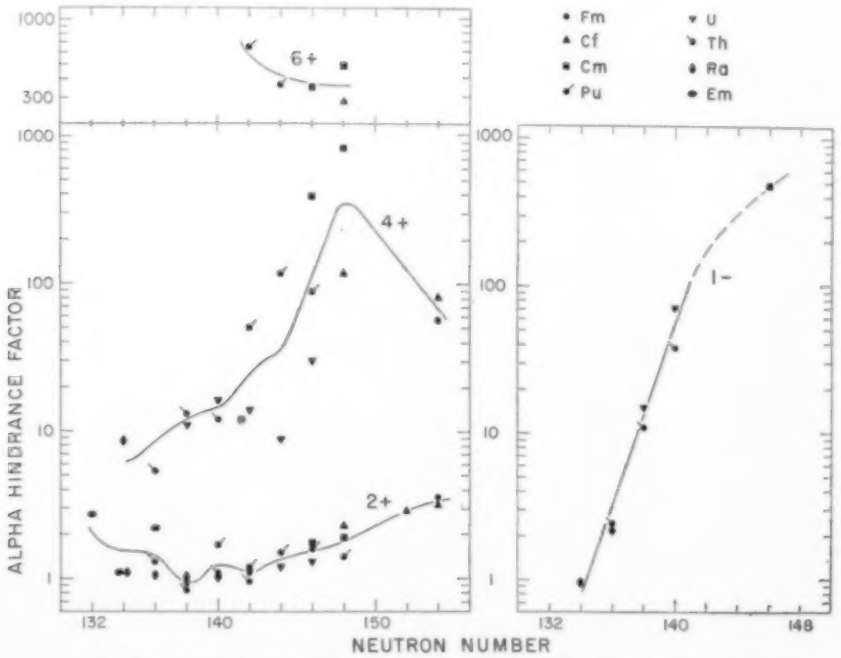


FIG. 8.—Hindrance factor as a function of neutron number for decay to excited states in even-even nuclei. (a) Even parity, even spin final states. (b) Odd parity, spin 1 final states.

understood. A discussion of several special cases exhibiting small hindrance appears in reference 7.

To obtain the basis for calculation of hindrance factors for odd-$Z$ nuclei, the constants $A$ and $B$ were averaged for adjacent even atomic numbers. The slope and

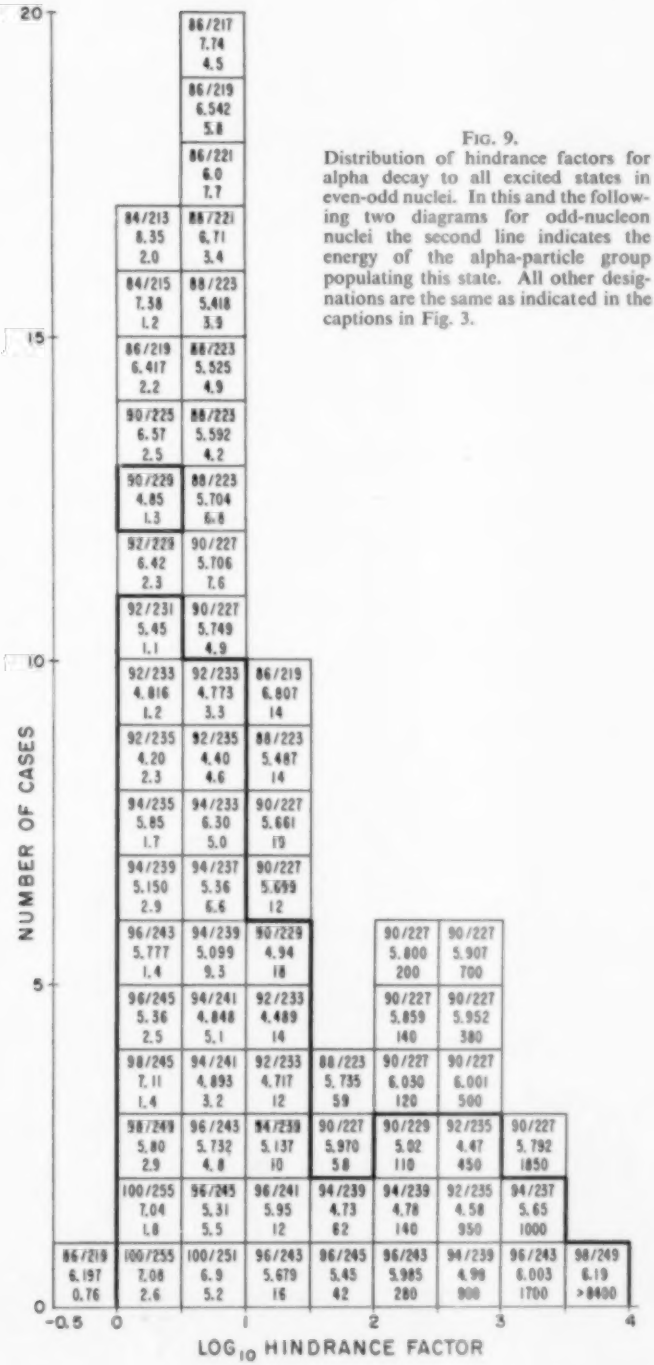


FIG. 9.
Distribution of hindrance factors for alpha decay to all excited states in even-odd nuclei. In this and the following two diagrams for odd-nucleon nuclei the second line indicates the energy of the alpha-particle group populating this state. All other designations are the same as indicated in the captions in Fig. 3.

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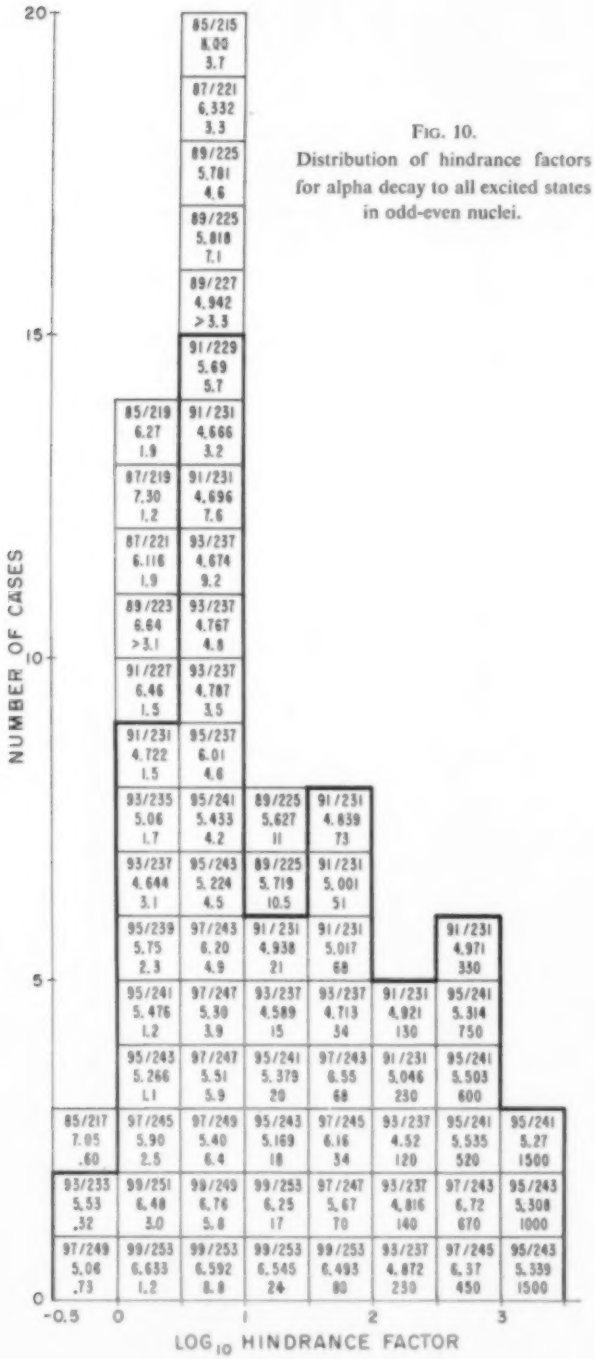


FIG. 10.
Distribution of hindrance factors for alpha decay to all excited states in odd-even nuclei.

intercept for einsteinium were obtained in the same manner as they were for fermium, by extrapolation. The constants so obtained are listed in Table 2.

Because the energies of the states in odd-nucleon nuclei populated by alpha decay have not been determined with certainty in many cases, we have indicated the energy of the alpha particle instead of the excited-state energy on the second line in the odd nucleon hindrance-factor histograms.

TABLE 2.—INTERPOLATED SEMI-EMPIRICAL CONSTANTS* FOR HINDRANCE FACTOR CALCULATIONS

| Element | *A* | *B* |
|---|---|---|
| 99 E | 155·04† | −53·3141† |
| 97 Bk | 152·65 | −53·3166 |
| 95 Am | 149·33 | −52·8862 |
| 93 Np | 146·86 | −52·8732 |
| 91 Pa | 145·84 | −53·4604 |
| 89 Ac | 141·68 | −52·7060 |
| 87 Fr | 138·31 | −52·3037 |
| 85 At | 133·40 | −51·1913 |

* Constants for the even-$Z$ elements are listed in Table 1. The constants are for use in equation (3), where $t_{1/2\alpha}$ is in seconds and $Q_{eff}$ is in MeV.

† Extrapolated values.

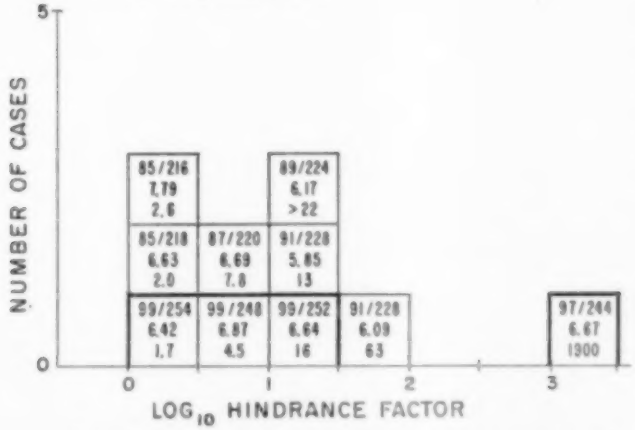


FIG. 11.—Distribution of hindrance factors for alpha decay to all excited states in odd-odd nuclei.

What can be said about the general form of the hindrance-factor distributions? It was hoped when this work was undertaken that histogram distributions of hindrance factors might exhibit a definite break-up into groups analogous to behaviour of the histograms of *ft* values in beta decay. Such does not seem to be the case here. The distributions peak for hindrance factors between 1 and 3 show very few cases with hindrance factors less than unity, and fall off fairly regularly as one proceeds out to the largest hindrance factors measured (of order 10,000). The fall-off of the distributions

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is, of course, largely a function of the increasing experimental difficulties of detecting the weaker alpha groups of a given isotope. A considerable number of highly hindered groups were found only by very careful experiments.

Among the isotopes of neutron number greater than 138 a parity change in alpha decay is often accompanied by a large (>100) hindrance factor, but this rule has at least one known exception (in $Cm^{243}$).

Many of the alpha groups which are virtually unhindered have been classified as "favoured" and are thought to be cases in which the initial and final wave functions of the odd nucleon are nearly the same.

We hope that the presentation of the rate data in histogram form can serve as a useful reference for further studies.

*Acknowledgements*—We are indebted to Dr. FRANK ASARO and Dr. FRANK STEPHENS and to JOHN HUMMEL, ALBERT GHIORSO, and others for valuable data in advance of publication. This study was carried out under the auspices of the US Atomic Energy Commission.

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 345 to 348. Pergamon Press Ltd., London

# RADIOCHEMICAL MEASUREMENT OF THE NATURAL FISSION RATE OF URANIUM AND THE NATURAL OCCURRENCE OF $Ba^{140}$

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(*Received* 10 *July* 1956)

**Abstract**—$Ba^{140}$ was isolated from 4540 g of uranyl acetate. The equilibrium amount of $Ba^{140}$ in the uranium salt was found to be $(1{\cdot}6 \pm 0{\cdot}1) \times 10^{-14}$ c $Ba^{140}$ per gram $U^{238}$, corresponding to an overall natural fission half-life of uranium of $(5{\cdot}9 \pm 0{\cdot}4) \times 10^{15}$ years, assuming a fission yield of 6·1% for $Ba^{140}$.

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## INTRODUCTION

THE occurrence of radioactive fission products in natural and in purified uranium-bearing materials is of interest in (a) determining the rate of spontaneous fission, and perhaps eventually the structure of the spontaneous fission-yield curve, and in (b) estimating the contribution of neutron-induced fission to the total fission pattern.

The present paper describes the radiochemical determination of the natural fission product $Ba^{140}$ in nonirradiated uranium salts. It is interesting to note that essentially the same experiment with a negative result has been described by HAHN and STRASSMANN,[1] who reported that the barium fraction from 10 g of nonirradiated uranium salt showed 14 c.p.m. of activity, in their historical paper on the discovery of fission in 1939.

The amount of $Ba^{140}$ expected to be present in nonirradiated uranium salts can be calculated according to the following equation.

$$Ba^{140}/U^{238}\ (c/c) = T_{1/2\alpha}/T_{1/2f} \cdot y \qquad (1)$$

where $T_{1/2\alpha}$ is the alpha decay half-life, $T_{1/2f}$ is the spontaneous fission half-life of $U^{238}$, and $y$ is the spontaneous fission yield of $Ba^{140}$. The actual amount of $Ba^{140}$ may be slightly higher than that obtained from equation (1), because of the contribution of neutron-induced fission. The value of $y$ is unknown, but let us assume that it is the same as the neutron-induced fission yield of $Ba^{140}$ (6·1%), for the time being.

Simple calculation yields a value of $1{\cdot}1_6 \times 10^{-13}$ c $Ba^{140}$ per 10 g $U^{238}$, or $1{\cdot}1_6 \times 10^{-11}$ c $Ba^{140}$ per 1000 g $U^{238}$.

## EXPERIMENTAL METHOD AND RESULTS

A total of 4540 g of uranyl acetate, $UO_2(C_2H_3O_2)_2{\cdot}2H_2O$, was dissolved in 7 litres of dilute nitric acid. Barium nitrate (880 mg) was added to the uranium solution and barium sulphate was precipitated by the addition of 35 ml of concentrated sulphuric acid. The precipitate of barium sulphate was filtered, dried, ignited in a porcelain crucible, and fused with 3 g of anhydrous sodium carbonate. The melt was leached

* This work was supported in part by the U.S. Atomic Energy Commission.

[1] O. HAHN and F. STRASSMANN *Naturwiss* **27**, 11 (1939).

with hot water and the residue was dissolved in a small volume of dilute hydrochloric acid. The sample was decontaminated by repeated additions of iron carrier, followed by ferric-hydroxide precipitation, and finally precipitated as barium carbonate. The barium-carbonate precipitate was filtered off, dissolved in a small volume of dilute hydrochloric acid, the solution evaporated to almost dryness, and then treated with 10 ml of concentrated nitric acid. The barium-nitrate precipitate was filtered, washed with concentrated nitric acid, and converted to the carbonate. The above-mentioned procedure was repeated several times, until the decontamination was complete.

The barium was then precipitated as the carbonate and mounted on aluminium for measurement with an end-window Geiger tube. Recovery of the barium carrier was 25%.

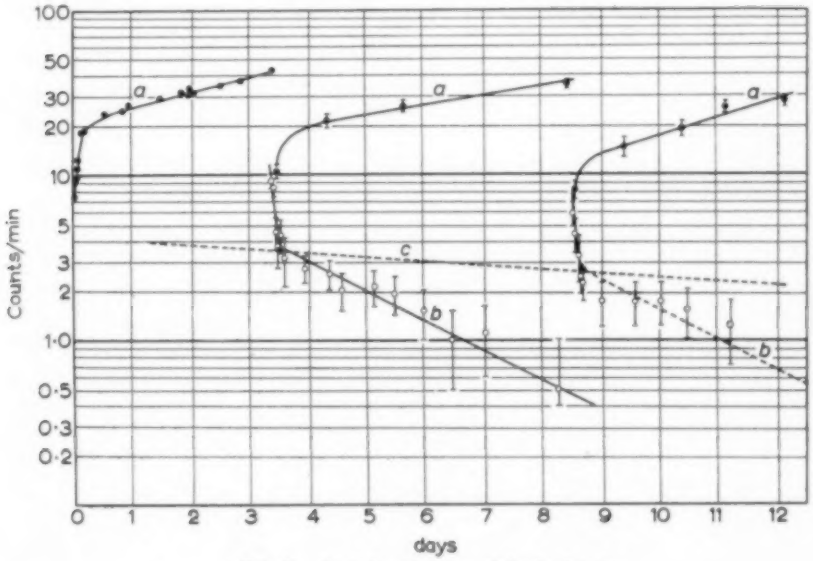


FIG. 1.—Growth and decay of the Ba fraction.
(a) Growth of $La^{140}$ + Rn and An daughters.
(b) Decay of $La^{140}$.
(c) Decay of $Ba^{140}$.

Results of the radioactivity measurements are shown in Fig. 1. The initial sharp rise is due to the growth of the 36-m $Pb^{211}$ (Ac*B*) from $Ra^{223}$ (Ac*X*) and the succeeding gradual rise is due to the growth of the 3·825-d $Rn^{222}$ from $Ra^{226}$ and the 40-hr $La^{140}$ from $Ba^{140}$. After about 90 hr (more than two half-lives of $La^{140}$), $La^{140}$ was separated from the barium carbonate as follows:

The barium carbonate was dissolved in a small volume of dilute nitric acid, boiled for a few minutes, 20 mg of ferric chloride was added to the solution and the iron precipitated with ammonium hydroxide. The precipitate was dissolved in nitric acid, 20 mg of neodymium nitrate carrier was added and neodymium oxalate was precipitated with oxalic acid. The neodymium oxalate was mounted on aluminium for measurement with an end-window Geiger tube. The initial rapid decay of the neodymium oxalate activity is due to the short-lived daughters of $Ra^{223}$ and $Ra^{226}$.

The $La^{140}$ separation was repeated again about 120 hr (three half-lives of $La^{140}$) after the first separation, as shown in Fig. 1.

From the average value of the $La^{140}$ activities observed, the equilibrium amount of $Ba^{140}$ in the original uranium salt (solid) was calculated to be $(1{\cdot}6 \pm 0{\cdot}1) \times 10^{-14}$ c $Ba^{140}$ per gram $U^{238}$, corresponding to an overall fission half-life of $(5{\cdot}9 \pm 0{\cdot}4) \times 10^{15}$ years, assuming a fission yield of 6·1% for $Ba^{140}$. This value agrees very well with the value obtained from the $Sr^{90}/U^{238}$ ratio in Great Bear Lake pitchblende by the authors in 1954.[2] Fig. 2 shows the results obtained with 2730 g of uranyl nitrate

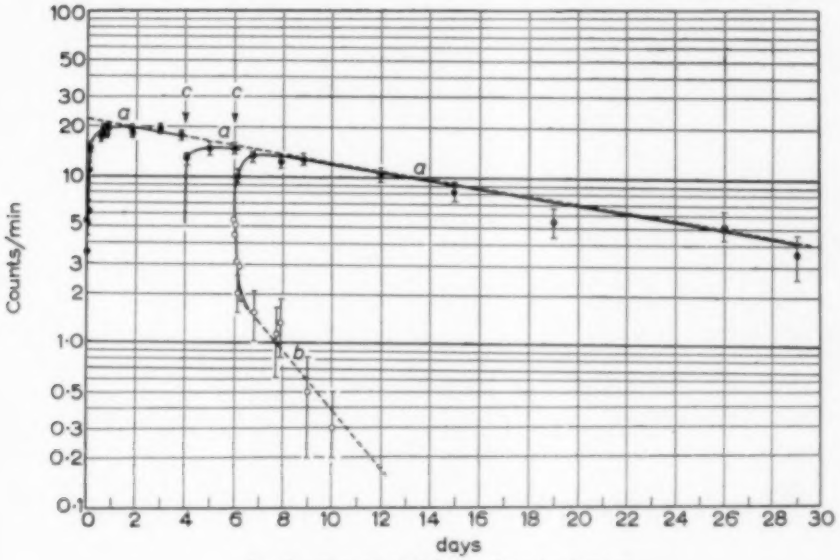


FIG. 2.—Growth and decay of the Ba fraction.
(a) Decay of $Ba^{140}$ plus $Ra^{223}$.
(b) Decay of $La^{140}$ separated from $BaCO_3$.
(c) Time of $La^{140}$ separation.

in aqueous solution, from which the isotopes of radium and barium had been initially removed, and the resulting uranium solution stored for 32 days. The growth and decay of $Ba^{140}$ formed from uranium, and $Ra^{223}$ formed from $Th^{227}$ during the 32 days are shown, and the absence of $Ra^{226}$ is obvious. Because of the small activity of $La^{140}$ observed, calculation of the overall natural fission rate of uranium has not been made, although the order of magnitude was found to be the same as the result reported above for uranyl acetate.

The discrepancy between the value of an overall fission half-life of uranium, $(5{\cdot}9 \pm 0{\cdot}4) \times 10^{15}$ years, radiochemically obtained by the authors, and the value of the spontaneous fission half-life of $U^{238}$, $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years, obtained by SEGRÈ[3] by the direct counting method, may be due either to (a) the contribution of neutron-induced fission, or (b) the difference in spontaneous fission and neutron-induced fission yields of $Ba^{140}$. If we assume that (a) is the case, the contribution of neutron-induced fission in solid uranyl acetate is estimated to be about 25%, whereas

[2] P. K. KURODA and R. R. EDWARDS *J. Chem. Phys.* **22**, 1940 (1954).
[3] E. SEGRÈ *Phys. Rev.* **86**, 21 (1952).

if (b) is the case, the spontaneous fission yield of $Ba^{140}$ must be about 8·3% instead of 6·1%.

The contribution of neutron-induced fission in natural uranium minerals has been shown by the mass spectroscopic measurements of WETHERILL,[4] and of THODE and co-workers,[5, 6] as well as the radiochemical measurements of KURODA and EDWARDS.[2] The result of the radiochemical measurements does not seem to contradict the mass-spectroscopic data. WETHERILL reported that about 35% of the fission in Belgian Congo pitchblende (44% U) is neutron-induced, while the authors found that about 27% of the fission in Great Bear Lake pitchblende (35% U) is neutron-induced.

Further experiments with more accurate low-level counting equipments are contemplated.

Since the abundance of uranium in average igneous rocks is 4 grams per ton, the abundance of the spontaneous fission product $Ba^{140}$ in igneous rocks is calculated to be $6{\cdot}4 \times 10^{-14}$ c per ton. It is interesting to note that the same order of magnitude of $Tc^{99}$ and $Pm^{147}$ should be present in igneous rocks. Since the fission yields of $Tc^{99}$ and $Pm^{147}$ are 6·2% and 2·6%, respectively, the abundance of $Tc^{99}$ and $Pm^{147}$ in average igneous rocks is calculated to be about $6{\cdot}5 \times 10^{-14}$ c and $2{\cdot}7 \times 10^{-14}$ c per ton, respectively.

It has to be pointed out, however, that appreciable amounts of artificially produced $Ba^{140}$ and other fission products are also present in nature. As an example, the presence of about $2{\cdot}5 \times 10^{-12}$ c $Ba^{140}$ per litre of rain water was observed in June 1953 at Fayetteville, Arkansas.[7]

[4] G. W. WETHERILL *Phys. Rev.* **92,** 907 (1953).
[5] W. H. FLEMING and H. G. THODE *Phys. Rev.* **92,** 378 (1953).
[6] J. MCNAMARA and H. G. THODE *Phys. Rev.* **80,** 471 (1950).
[7] P. E. DAMON and P. K. KURODA *Nucleonics* **11,** 59 (1953).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 349 to 356. Pergamon Press Ltd., London

# SOME PHYSICAL PROPERTIES OF MOLTEN AND SUPERCOOLED GALLIUM TRICHLORIDE

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(*Received* 24 *August* 1956)

**Abstract**—The viscosity of molten gallium trichloride has been measured both above and below the melting-point, and a small discontinuity in slope of the log $\eta - 1/T$ curve has been found near the melting-point despite the symmetrical and nonpolar nature of the gallium-trichloride dimer. The density and surface tension have also been determined over a range of temperature and the results used to calculate the parachor and related properties of the compound.

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## INTRODUCTION

OBSERVATIONS on supercooled ionic liquids as well as on liquids containing unsymmetrical or polar molecules have shown that the temperature dependence of certain properties changes discontinuously in the region of the melting-point.[1] Fewer data are available on nonpolar liquids, but the recent work of ROBERTS[2] on the dielectric polarization of symmetrical aromatic hydrocarbons suggests that the magnitude of the change in slope is related to the dipole moment and is zero for compounds such as benzyl benzene, dibenzyl, and *p*-xylene. Gallium trichloride in the liquid phase consists of molecules in which $GaCl_3$-monomers are joined by bridging chlorine atoms to form symmetrical $Ga_2Cl_6$-dimers.[3] Since, moreover, gallium trichloride can readily be supercooled some 12° below its m.p., 77·75°, it seemed a convenient compound to investigate in the supercooled region. The viscosity was also required as part of a larger investigation into the physical properties of the addition compounds which gallium trichloride forms.[4] Subsidiary data which were needed on the density of gallium trichloride were determined in such a way as to give simultaneously an approximate value of the surface tension. Although neither density nor surface tension show the type of discontinuity observed for dielectric constant or activation energy of viscous flow,[1] the measurements are of interest in being apparently the only determination of the surface tension of a compound of gallium; they therefore lead for the first time to an experimental value for the atomic parachor of gallium.

## EXPERIMENTAL

Gallium trichloride was prepared from high-purity gallium metal and purified by vacuum sublimation in the way already described.[4] It formed large, beautifully shaped, transparent crystals which melted sharply at 77·75 ± 0·05°.

Viscosity was measured in the apparatus shown in Fig. 1. The capillary viscometer, which was sealed off at point 3, was designed to measure the viscosity of hygroscopic, reactive, or volatile liquids over a range of temperature, and has been fully discussed elsewhere.[5] The liquid was timed as its

[1] N. N. GREENWOOD and R. L. MARTIN *Proc. Roy. Soc.* **A215**, 46 (1952).
[2] G. N. ROBERTS *J. Amer. Chem. Soc.* **75**, 2264 (1953).
[3] H. GERDING *J. Chim. phys.* **46**, 118 (1948); H. GERDING, H. G. HARING, and P. A. RENES *Rec. trav. chim.* **72**, 78 (1953).
[4] N. N. GREENWOOD and K. WADE *J. Chem. Soc.* 1527 (1956).
[5] N. N. GREENWOOD and K. WADE *J. Appl. Chem.* in the press.

upper surface passed the etched marks *B* and *C*, the lower surface being maintained at a constant level by means of the weir *A* over which the liquid flowed into the sump *D*. The mean head of liquid was therefore independent of the volume, provided that this was not so great as to fill the sump. The viscometer was calibrated by means of aniline in the temperature range 50–100°, and the kinematic viscosity $\nu$ was found to be related to the efflux time $t$, by the equation

$$\nu = 3{\cdot}535 \times 10^{-3}t - 2{\cdot}20/t.$$

For gallium trichloride this time varied between 200 and 300 sec in the temperature range studied, and was measured on a calibrated stopwatch reading to 0·1 sec.

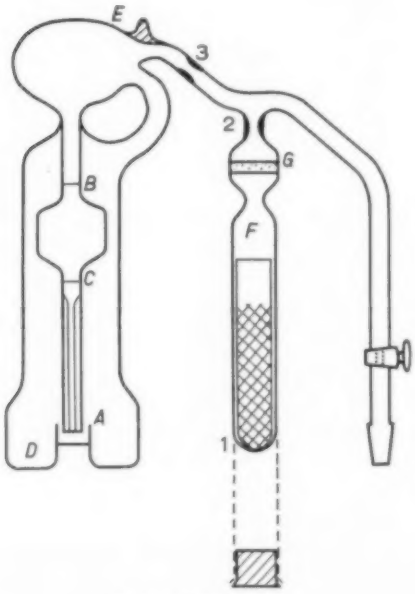


FIG. 1.—Viscometer.

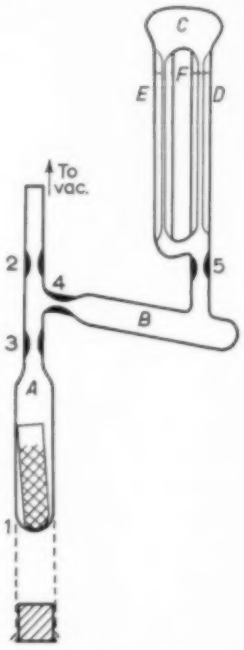


FIG. 2.—Dilatometer.

To load the viscometer at the start of a temperature run, resublimed gallium trichloride was sealed into the tube *F* by drawing it off at position 1. The whole apparatus was then inverted and, after the compound had been melted, it was drawn through the sintered glass disc *G* by evacuating the viscometer. This precaution was taken to remove any splintered or powdered glass which might inadvertently have got into the gallium trichloride when the sample tube was opened. The sintered glass disc was then drawn off at point 2, and the liquid was thoroughly degassed under hard-vacuum before being finally sealed in the viscometer at the constriction 3.

The thermostat consisted of an oil-bath in a large unsilvered Dewar flask; it was electrically heated and stirred, and the temperature was maintained constant to ±0·01° by means of a manually adjusted Variac transformer. Temperatures were read to 0·02° on a mercury thermometer which had been calibrated directly against NPL standard thermometers at 5° intervals.

Density was measured by means of the dilatometer shown in Fig. 2. This comprised a bulb *C* of about 2·5-ml capacity on to which were sealed two capillary tubes, *D*, *E*, of radius 0·8452 mm and 0·3470 mm. The radii of the capillaries and their uniformity were determined by measuring the lengths occupied by known weights of mercury. The volume of the dilatometer up to the etched marks *F* was determined in the temperature range 0–150° by means of several experiments with degassed mercury, the usual corrections being applied for buoyancy and thermal expansion of glass.

To measure the density of gallium trichloride, a sample was placed in tube *A*, Fig. 2, which was

drawn off at point 1 as shown. After thorough evacuation, the apparatus was sealed at 2 and the gallium trichloride sublimed into compartment *B* which was then drawn off at constriction 4. After being remelted at 82°, the compound was poured into the dilatometer, which was then sealed at point 5. It was found that the double capillary facilitated the loading of the dilatometer even when the whole apparatus was evacuated. At the conclusion of a temperature run, during which the heights of the menisci and etched marks were measured at each temperature on a precision cathetometer (0·01 mm), the dilatometer and its contents were weighed. The apparatus was then carefully broken open near point 5 and the pieces reweighed after emptying and cleaning to get the weight of gallium trichloride used.

By having the two capillaries of different radius it was possible to estimate the surface tension simultaneously with the density. However, to obtain density results over the required temperature range, it was necessary to have fairly wide-bore capillaries, and consequently the values for the surface tension have not the precision that might otherwise have been achieved by this method. Nevertheless, they give a valuable indication of the magnitude of the surface tension of gallium trichloride and of its variation with temperature. The difference in capillary rise for gallium trichloride in the apparatus was about 4–5 mm, and heights were corrected for the meniscus by means of the formula:

$$h = h_0 + (r/3) - (0{\cdot}1288r^2/h_0) + (0{\cdot}1312r^3/h_0^2).$$

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## RESULTS

The kinematic viscosity ($\nu$ centistoke), dynamic viscosity ($\eta$ centipoise), and fluidity ($\phi$ cp$^{-1}$) of gallium trichloride in the temperature range 66–90° are presented in Table 1. The relation between these three quantities and the density ($d$ g ml$^{-1}$) is:

$$\eta = \nu \,.\, d = 1/\phi.$$

When log $\eta$ is plotted against the reciprocal of the absolute temperature (see Fig. 3), the points fall unmistakably on two straight lines which intersect at 81°. Above the m.p. the slope corresponds to an activation energy of viscous flow $E = 3{\cdot}63_4$ kcal mole$^{-1}$; below this temperature the value is $3{\cdot}86_2$ kcal mole$^{-1}$, an increase of 6·2%. It is not possible to fit the points with the same precision either by a single straight line or by a continuous curve.

TABLE 1.—VISCOSITY AND FLUIDITY OF GALLIUM TRICHLORIDE

| $t$° | $\nu$ (cs) | $\eta$ (cp) | $\phi$ (cp$^{-1}$) | $t$° | $\nu$ (cs) | $\eta$ (cp) | $\phi$ (cp$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 67·10 | 1·045 | 2·170 | 0·4608 | 78·18 | 0·8821 | 1·811 | 0·5523 |
| 68·10 | 1·029 | 2·133 | 0·4688 | 79·19 | 0·8692 | 1·783 | 0·5610 |
| 69·10 | 1·012 | 2·097 | 0·4769 | 80·20 | 0·8567 | 1·755 | 0·5698 |
| 70·10 | 0·9964 | 2·062 | 0·4849 | 81·21 | 0·8443 | 1·716 | 0·5788 |
| 71·11 | 0·9812 | 2·029 | 0·4929 | 82·22 | 0·8324 | 1·702 | 0·5876 |
| 72·12 | 0·9657 | 1·995 | 0·5014 | 83·24 | 0·8210 | 1·677 | 0·5964 |
| 73·13 | 0·9513 | 1·963 | 0·5095 | 84·25 | 0·8096 | 1·652 | 0·6055 |
| 74·14 | 0·9370 | 1·931 | 0·5178 | 85·26 | 0·7990 | 1·628 | 0·6141 |
| 75·15 | 0·9228 | 1·900 | 0·5263 | 86·28 | 0·7885 | 1·605 | 0·6230 |
| 76·16 | 0·9089 | 1·870 | 0·5349 | 87·29 | 0·7781 | 1·582 | 0·6320 |
| 77·17 | 0·8953 | 1·840 | 0·5436 | 88·30 | 0·7677 | 1·560 | 0·6412 |
| 77·75 | | melting-point | | 90·33 | 0·7484 | 1·517 | 0·6591 |

An alternative method of plotting the data[1] is to use BATSCHINSKI's equation relating the specific volume $v$ ml g$^{-1}$ to the fluidity:

$$v = b + B\phi$$

where $b$ and $B$ are constants. When the specific volume is plotted against fluidity, the points again fall on two straight lines intersecting near the m.p. Above this temperature the slope $B$ is 0·0575 ml gm$^{-1}$ cp; in the supercooled region it is 0·0597 ml gm$^{-1}$ cp, an increase of 3·9%. The point

of intersection is 75·5°, that is, about the same distance below the m.p. as the previous discontinuity was above it. However, there is no theoretical reason to suppose that the two discontinuities should occur exactly at the same temperature or that these should correspond precisely to the m.p. The results do suggest, however, that at least in this instance, the absence of a dipole moment in a molecule, though perhaps reducing the magnitude of the discontinuity in slope, has not resulted in complete suppression of the effect.

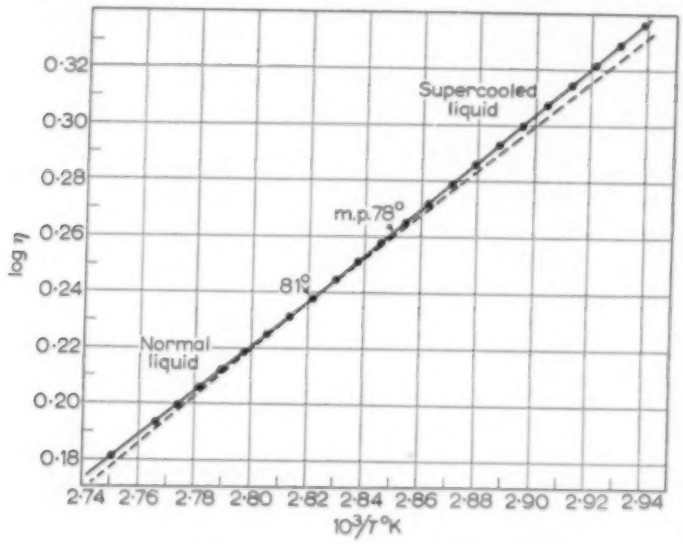


FIG. 3.—Viscosity of molten gallium trichloride.

The density of molten gallium trichloride in the temperature range 71–140° is given in Table 2. The results may be represented to within 2 in the last figure by the equation

$$d_4^t = 2{\cdot}0531 - 0{\cdot}00209(t - 78).$$

TABLE 2.—DENSITY AND SURFACE TENSION OF GALLIUM TRICHLORIDE

| $t°$ | $d_4^t$ (g ml$^{-1}$) | $V_M$ (ml mole$^{-1}$) | $\gamma$ (dyne cm$^{-1}$) | $\omega = \gamma V_M^{2/3}$ | $[P] = V_M\gamma^{1/4}$ |
|---|---|---|---|---|---|
| 71·0 | 2·0678 | 170·32 | 28·10 | 863·4 | 392·0 |
| 75·15 | 2·0591 | 171·04 | 27·69 | 853·1 | 392·2 |
| 80·05 | 2·0488 | 171·90 | 27·08 | 837·0 | 392·1 |
| 84·0 | 2·0397 | 172·66 | 26·66 | 826·6 | 392·3 |
| 90·1 | 2·0278 | 173·68 | 25·98 | 808·7 | 392·0 |
| 95·0 | 2·0178 | 174·54 | (25·03) | (781·8) | (390·4) |
| 98·1 | 2·0107 | 175·15 | 24·95 | 780·9 | 391·4 |
| 105·1 | 1·9964 | 176·41 | 24·36 | 766·3 | 391·8 |
| 110·2 | 1·9857 | 177·36 | 24·06 | 759·5* | 392·7 |
| 114·95 | 1·9757 | 178·26 | 23·43 | 742·0 | 392·1 |
| 119·8 | 1·9659 | 179·15 | 22·98 | 730·2 | 392·1 |
| 124·5 | 1·9560 | 180·05 | 22·35 | 712·5 | 391·4 |
| 129·5 | 1·9460 | 180·98 | 21·96 | 702·5 | 391·9 |
| 135·3 | 1·9334 | 182·16 | (21·70) | (697·2) | (393·0) |
| 140·3 | 1·9226 | 183·18 | (21·30) | (686·9) | (393·4) |

At the m.p. (77·75°) this corresponds to a density of 2·0536 gm ml$^{-1}$ and a molar volume $V_M$ for the molecule $Ga_2Cl_6$ of 171·44 ml mole$^{-1}$.

The surface tension, which is also given in Table 2, is somewhat less precise for the reasons already outlined, but may be represented to within 0.1 dyne cm$^{-1}$ by the equation

$$\gamma = 27{\cdot}3_0 - 0{\cdot}105(t - 78).$$

From these values of the density and surface tension the molar surface free energy ($\omega$ erg mole$^{-2/3}$) may be computed from the relation

$$\omega = \gamma V_M^{2/3}$$

The values range from 863 erg mole$^{-2/3}$ at 71° to 687 erg mole$^{-2/3}$ at 140°, and may be represented by the equation

$$\omega = 841{\cdot}8 - 2{\cdot}70(t - 78)$$

in which the Eötvös constant $k$ is 2·70.

The parachor of gallium trichloride has been calculated from the expression

$$[P] = \frac{M\gamma^{1/4}}{(d_{liq} - d_{gas})} \simeq \frac{M\gamma^{1/4}}{d_{liq}} = V_M\gamma^{1/4}.$$

Neglect of the gas density reduces the parachor by less than one part per thousand below 130° and, as this is within the experimental error, the simpler formula has been used. It will be seen from Table 2 that the parachor is constant throughout the temperature range investigated.

## DISCUSSION

The physical properties of molten gallium trichloride at the m.p. are summarized in Table 3. The only data which can be compared with earlier work concern the

TABLE 3.—PHYSICAL PROPERTIES OF MOLTEN GALLIUM TRICHLORIDE AT THE M.P., 77·75°

| | |
|---|---|
| mol. wt. ($Ga_2Cl_6$) | 352·18 |
| $d$ (g ml$^{-1}$) | 2·0536, $(2{\cdot}06_2)$[6] |
| temp. coeff. of $d$ | $2{\cdot}09 \times 10^{-3}$, $(2{\cdot}0_5 \times 10^{-3})$[6] |
| $V_M$ (ml mole$^{-1}$) | 171·44 |
| $\nu$ (cs) | 0·8877 |
| $\eta$ (cp) | 1·823 |
| $E_\eta$ (kcal mole$^{-1}$) | $3{\cdot}63_0$; $3{\cdot}86_2$ (supercooled) |
| $\phi$ (cp$^{-1}$) | 0·5486 |
| $B$ (ml g$^{-1}$ cp) | $5{\cdot}75 \times 10^{-3}$; $5{\cdot}97 \times 10^{-3}$ (supercooled) |
| $\gamma$ (dyne cm$^{-1}$) | $27{\cdot}3_2$ |
| temp. coeff. of $\gamma$ | 0·105 |
| $\omega$ (erg mole$^{-2/3}$) | 842·5 |
| $k$ (erg mole$^{-2/3}$ deg$^{-1}$) | 2·70 |
| $[P]$ (ml dyne$^{1/4}$ cm$^{-1/4}$ mole$^{-1}$) | 392·0 |
| $\kappa$ (ohm$^{-1}$ cm$^{-1}$) | $1{\cdot}86 \times 10^{-6}$[7] |
| vap. press. (mm Hg) | $10{\cdot}4$[1,8] |
| $\Delta H_{vap}$ (kcal mole$^{-1}$) | 11·8[8], 12·3[9] |
| $\Delta H_{fus}$ (kcal mole$^{-1}$) | 5·2[8] |

[6] W. KLEMM and W. TILK *Z. anorg. Chem.* **207**, 161 (1932).
[7] N. N. GREENWOOD and I. J. WORRALL *J. Inorg. Nucl. Chem.* **3**, 351 (1956).
[8] A. W. LAUBENGAYER and F. B. SCHIRMER *J. Amer. Chem. Soc.* **62**, 1578 (1940).
[9] W. FISCHER and O. JÜBERMANN *Z. anorg. Chem.* **227**, 227 (1936); and **215**, 254 (1940).



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density for which KLEMM and TILK[6] found $d_4^t = 2{\cdot}06_3 - 0{\cdot}0020_5\ (t - 78)$, in reasonable agreement with the present values.

The occurrence of discontinuities in the temperature dependence of certain physical properties of ionic and polar liquids in the region of their m.p. has been discussed in a previous review,[1] which stressed the need for similar measurements on symmetrical and nonpolar liquids as well. In polar liquids, discontinuities have been observed in the appropriate functions with temperature of viscosity, electrical conductivity, dielectric constant, and ultrasonic wavelength, but no change was detected in density, surface tension, or vapour pressure. The present investigation demonstrates the presence of a discontinuity in the plot of log $\eta$ versus $1/T$ for gallium trichloride which is composed of symmetrical dimeric molecules.[3] It may be concluded, therefore, that the presence of a dipole moment in the molecule is not necessary for the effect, at least when viscosity is the property being investigated. This conclusion differs from the one drawn by ROBERTS[2] on the basis of dielectric polarization measurements on symmetrical aromatic hydrocarbons, and for this reason viscosity determinations are being made on the particular compounds used by him in order to discover whether, in fact, the discontinuity is suppressed for viscosity as well as for dielectric constant. Ultrasonic measurements would also be instructive, but electrical conduction would hardly be relevant for such compounds.

An alternative interpretation of the discontinuities observed in the present experiments is that the effect is spurious. However, the discontinuity is not due to instrumental peculiarities, since other liquids such as water and aniline when measured in the same viscometer and with the same thermometers and stop-watch gave smooth Arrhenius plots. Moreover, gallium trichloride showed the same behaviour near the melting-point when a second viscometer was used. Nor can the discontinuity be ascribed to contamination, since the apparatus was dried thoroughly under vacuum before use and was loaded by vacuum techniques.

A discontinuity was also found when the specific volume was plotted against fluidity. In this case the slope of the curve gives BATSCHINSKI's constant $B$, which is related to the size of the flow unit in the liquid.[10] The increase in slope on supercooling would therefore imply a slight increase in the size of these units due, presumably, to partial aggregation. It is interesting to note that the values of $B$ (in ml $g^{-1}$ cp $\times 10^{-2}$) obtained for dimeric gallium trichloride (5·75 and 5·97) are similar to those of moderately small organic molecules which might be expected to have about the same volume, e.g. diethyl ether (5·71), ethyl formate (5·67), *n*-propyl formate (5·76), and *n*-propyl ether (6·09); cf. methyl iodide (2·84) and *n*-octane (6·65).

The surface tension and related properties which are given in Table 2 are of interest in being the first such determinations on any compound of gallium. The molar surface free energy, $\omega$, decreases linearly with rise in temperature; at the critical point the meniscus would disappear and the molar surface free energy of the liquid would become zero. On the basis of such an extrapolation the critical point of gallium trichloride is estimated to be 390°. An independent estimate may be obtained from GULDBERG's rule that, on the absolute temperature scale, the boiling point occurs at two thirds of the critical temperature: as the b.p. is 200°C = 473°K,[8, 9] the critical temperature is 437°C, in reasonable agreement with the value

[10] B. S. HARRAP and E. HEYMANN *Chem. Rev.* **48**, 45 (1951).

deduced from the surface free energy. Neither value is likely to be very precise, because of the tendency of the dimer to dissociate in the gas phase at high temperatures. Thus, extrapolation of FISCHER and JÜBERMANN's data[9] to 400°C gives a critical pressure of 13,500 mm (17·8 atm) and a dissociation constant $Kp$ of 1315 mm, from which the degree of dissociation is 15·4%.

The final property to be discussed is the parachor. The data in Table 2 indicate that, between 70° and 130° the parachor is constant to within ±0·2%, the mean value being 392·0 ± 0·4 (S.D.). This constancy is, of course, independent of any attempt to treat the parachor as an additive molecular constant and, in fact, it is possible to devise an unlimited number of arbitrary but selfconsistent schemes for building up the molecular parachor from atomic and constitutional units.[11] On SUGDEN's scheme,[12] the atomic parachor of gallium may be calculated from the known dimeric structure of gallium trichloride by taking the parachor of chlorine as 54·3 and allowing 11·6 for the four-membered ring and −1·6 for each of the two co-ordinate bonds. This gives a value of 28·9 for gallium, which differs considerably from the value of 50 tentatively suggested by SUGDEN on the basis of the apparent surface tension of gallium metal. Since then it has been shown that the surface tension of highly purified gallium metal leads to a parachor value of 60·8;[13] this would not be expected to be the same as the value derived from gallium trichloride, since the bonding of gallium in the metallic state is not comparable with that in its covalent compounds. It should be remarked, however, that the systematic trends observed for the Sugden parachor values of atoms in groups III to VII of the periodic table would predict a value of about 45–48 for gallium in its covalent compounds. The slight uncertainty arises from an uncertainty in the experimental value for germanium,[12, 14, 15] but the predicted value is clearly some 17 units higher than the value calculated from the present experimental data.

An alternative method of deriving atomic parachors has been proposed by SAMUEL.[16] This allows for a variation in the parachor of an atom when its valency is altered, and overcomes the difficulty inherent in SUGDEN's scheme which necessitated the postulation of singlet links whenever exceptions to the octet rule were encountered. Applied to gallium trichloride, SAMUEL's method leads to an atomic parachor of 27·3 for gallium, the expected value being about 48. A similar discrepancy is obtained even when the most recent method due to MCGOWAN[17] is applied. This method uses a simpler and more direct approach than the other two, and generally gives excellent results. It predicts an atomic parachor for combined gallium of 99·0 units, but the value calculated from the present data is 86·0 on this scale. The reason for these large differences between predicted and calculated values is not clear. Experimental errors in the determination of surface tension could not account for such discrepancies, since errors of the order of 25% would be required. Nor does the assumption of alternative structures for gallium trichloride (monomer, trimer, etc.) resolve the difficulty. It may, however, be relevant that the molecular parachor

[11] A. SIPPEL *Ber.* **63**, 2185 (1930).
[12] S. SUGDEN *The Parachor and Valency* Routledge, London. 1929; *Thorpe's Dict. of Appl. Chem.* 4th Ed., Longmans Green, London, **9**, 225 (1949).
[13] G. L. MACK, J. K. DAVIS, and F. E. BARTELL *J. Phys. Chem.* **45**, 846 (1941).
[14] N. V. SIDGWICK and A. W. LAUBENGAYER *J. Amer. Chem. Soc.* **54**, 948 (1932).
[15] T. G. PEARSON and P. L. ROBINSON *J. Chem. Soc.* 736 (1934).
[16] R. SAMUEL *J. Chem. Phys.* **12**, 167 (1944).
[17] J. C. MCGOWAN *Chem. and Ind.* 495 (1952).

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of compounds of aluminium[18, 19] can be reproduced with some precision by MCGOWAN's method when the predicted value of 84·9 for the atomic parachor of aluminium is used; exceptions only arise when ring structures are present, notably $Al_2Br_6$, for which the calculation is in error by 17 units.

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[18] S. SUGDEN *J. Chem. Soc.* 316 (1929).
[19] R. A. ROBINSON and D. A. PEAK *J. Phys. Chem.* **39**, 1125 (1935).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 357 to 364. Pergamon Press Ltd., London

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# IONIC AND COVALENT FORMS OF THE GALLIUM TRIHALIDES

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**Abstract**—The electrical conductivity of crystalline gallium tribromide increases rapidly with rise in temperature up to a maximum value of $16{\cdot}5 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 115°. About 3° below the m.p. (122·3°) the conductivity suddenly decreases, and this process continues as the compound melts, the conductivity passing through a minimum of $0{\cdot}72 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ some 2° above the m.p. This twenty-three-fold drop in conductivity at the melting-point is ascribed to a transformation from an ionic solid to a liquid which consists predominantly of dimeric $Ga_2Br_6$ molecules. Gallium trichloride (m.p. 77·75°) behaves similarly, the conductivity decreasing nine-fold from $15 \times 10^{-6}$ to $1{\cdot}7 \times 10^{-6}$ on melting. Gallium tri-iodide has a somewhat higher conductivity and does not show the effect: near the m.p. (211·5°) the solid has a conductivity of $56 \times 10^{-6}$; the conductivity of the liquid is $118 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$. Despite this increase in conductivity, it is shown that molten gallium tri-iodide, like the other two compounds, tends to favour the covalent form, the degree of ionization being much smaller than that in the solid state. The results are discussed and compared with earlier data on these and related compounds.

## INTRODUCTION

A COMPOUND need not have the same ionic or molecular structure in both the solid and the liquid phase. Phosphorus pentachloride has a three-dimensional ionic lattice built up of $PCl_4^+$ and $PCl_6^-$ units,[1] whereas the melt has negligible conductivity[2] and consists of $PCl_5$ molecules.[3] Aluminium trichloride has a two-dimensional ionic lattice[4] but again the conductivity of the compound drops at the m.p.[5] and in the molten state dimeric molecules $Al_2Cl_6$ predominate.[6] In both these examples an ionic solid melts to a covalent, molecular liquid. The reverse type of change is also known, since antimony trifluoride, which has a molecular lattice of $SbF_3$ units,[7] gives rise to a highly conducting ionic melt.[8] Iodine trichloride may provide another instance, the molecular lattice of $I_2Cl_6$ units[9] melting to an ionic liquid,[10] but in this case the handling of the compound entails considerable experimental difficulty and it is possible that the solid is, in fact, ionic and that the increase in conduction on melting[11] is merely the normal increase expected in ionic compounds due to the greater mobility of the ions in the liquid phase.

[1] D. CLARK, H. M. POWELL, and A. F. WELLS *J. Chem. Soc.* 642 (1942).
[2] A. VOIGT and W. BILTZ *Z. anorg. Chem.* **133**, 277 (1924).
[3] H. MOUREU, M. MAGAT, and G. WÉTROFF *Compt. Rend.* **205**, 276 (1937).
[4] J. A. A. KETELAAR, C. H. MACGILLAVRY, and P. A. RENES *Rec. trav. chim.* **66**, 501 (1947).
[5] W. BILTZ and A. VOIGT *Z. anorg. Chem.* **126**, 39 (1923).
[6] H. GERDING and E. SMIT *Z. phys. Chem.* **B50**, 171 (1941).
[7] A. BYSTROM and A. WESTGREN *Ark. Kem. Min.* **17B**, No. 2, 1 (1943).
[8] A. WOOLF *J. Chem. Soc.* **1955**, 279.
[9] K. H. BOSWIJK and E. H. WEIBENGA *Acta. Cryst.* **1**, 417 (1954).
[10] N. N. GREENWOOD and H. J. EMELÉUS *J. Chem. Soc.* 987 (1950).
[11] C. G. VONK, K. H. BOSWIJK, and E. WIEBENGA *Rec. trav. chim.* **74**, 897 (1955).

The electrical properties of the trihalides of gallium are somewhat uncertain. The molten trichloride has been reported[12] to have a specific conductivity of either $<10^{-7}$ or $<10^{-8}$ ohm$^{-1}$ cm$^{-1}$ and the molten tribromide as having a conductivity of $5 \cdot 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at the m.p. The same authors give the conductivity of the molten tri-iodide as $2 \cdot 10^{-2}$ ohm$^{-1}$ cm$^{-1}$ in a table and $(5–6) \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ in a graph, but mention that their data on this compound are unreliable.[12] The electrical conductivity of the trihalides in the solid state has not previously been reported. Since the conductivities of the trihalides were required as part of an investigation into the properties of their addition compounds, it was decided to reinvestigate them, using high-purity materials. During the course of this work the reversible transformation between ionic and covalent forms of the trichloride and tribromide was observed. The tri-iodide, which might at first appear from conductivity measurements to be essentially ionic in both the solid and the liquid phase, is also shown to favour covalency in the liquid phase.

## EXPERIMENTAL

Gallium trichloride was prepared and purified as described by GREENWOOD and WADE.[13] The m.p. was 77·75 ± 0·05°. Gallium tribromide was prepared by a method based on that of KLEMM and TILK.[12] Analar bromine, previously dried over phosphorus pentoxide and diluted with nitrogen

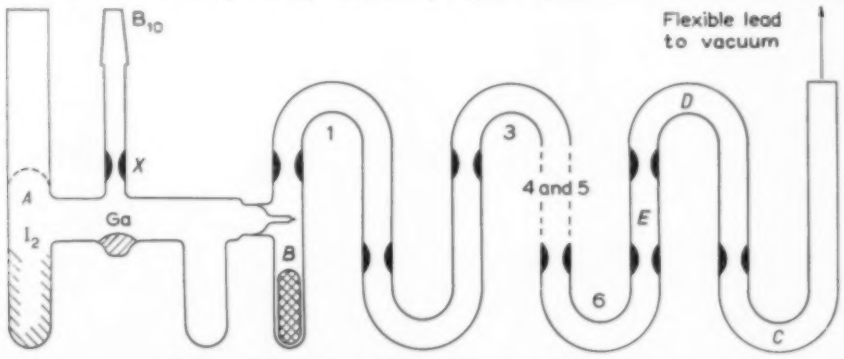


FIG. 1.—Preparation and purification of gallium tri-iodide.

which had been dried by passing it through a trap cooled in liquid air, was passed over high-purity gallium metal (15 g) heated to 130° in an oil-bath. The gallium tribromide so formed was purified by repeated vacuum sublimation at 150° in a separate all-glass apparatus. The pure, colourless compound melted sharply at 122·3 ± 0·05°. Literature values are 121·5 ± 0·6°,[14] 122·5°,[15] and 124·5 ± 0·5.[12]

Gallium tri-iodide was prepared by a modification of KLEMM and TILK's method.[12] Analar iodine, resublimed from potassium iodide, was placed in limb *A* of the apparatus shown in Fig. 1, which was then sealed as indicated. Gallium metal was placed in the central compartment of the reaction vessel, which was then evacuated and sealed at constriction *X*. Iodine vapour was repeatedly passed backwards and forwards over the warmed gallium until all the metal (2 g) had reacted. The magnetically operated breaker-seal *B* was then opened and the excess iodine removed by sublimation into trap *C*. The yellow gallium tri-iodide was purified by six successive sublimations at 160° in the 1-cm-diameter vacuum train shown, first fractions being driven through to the end traps *C* and *D* each time and last fractions being left in the heated limb, which was sealed off after each fractionation. The compound was finally sublimed into the sample tube *E*, which was sealed at both ends whilst still

[12] W. KLEMM and W. TILK *Z. anorg. Chem.* **207**, 161 (1932).
[13] N. N. GREENWOOD and K. WADE *J. Chem. Soc.* 1527 (1956).
[14] W. FISCHER and O. JÜBERMANN *Z. anorg. Chem.* **227**, 227 (1936).
[15] W. C. JOHNSON and J. B. PARSONS *J. Phys. Chem.* **34**, 1210 (1930).

under dynamic vacuum. The m.p. was 211·5 ± 0·1°; literature values are 210 ± 1°,[12] 213·5°,[15] and 214°.[16]

Three conductivity cells were made by sealing lengths of 1-mm-diameter tungsten rod into Pyrex tubing, electrical contact being obtained through pools of mercury in the side arms. The cell constants were measured at 25°, using aqueous solutions of potassium chloride, and were 0·183 $cm^{-1}$ for the trichloride cell, 0·246 $cm^{-1}$ for the tribromide, and 15·3 $cm^{-1}$ for the tri-iodide. The cells were loaded as shown in Fig. 2: the whole apparatus was thoroughly dried before each run by heating the electrode assembly in an oil-bath for several hours at 130° under vacuum and by simultaneously flaming out the rest of the apparatus. A sample tube of trihalide, which had been sealed under vacuum, was broken in air and placed quickly in tube *A*, which was closed with a guard tube of phosphorus pentoxide and drawn off. The apparatus was next evacuated and sealed at *B*. The trihalide was sublimed into the cell by placing limb *A* in an oil-bath at the appropriate temperature and the cell was finally drawn off at the constriction *C*.

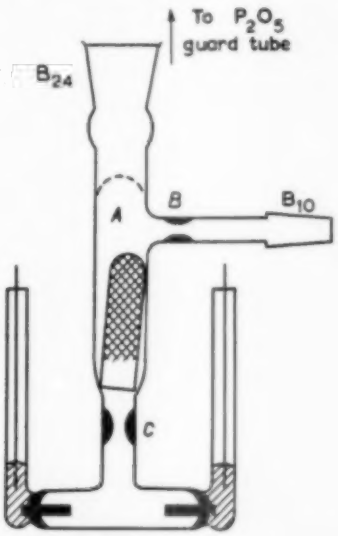


FIG. 2.—Conductivity cell.

The electrical conductivity was measured at 1000 cycles by means of a circuit similar to that described by GREENWOOD, MARTIN, and EMELÉUS.[17] The output from a variable beat-frequency oscillator (Marconi TF 195M) was fed into an earthed bridge network; the ratio arms were obtained on a precision two-dial box, each dial having nine steps between 1 and $10^4$ ohm (Muirhead 14-243-C); capacities were balanced by means of a set of radio-condensers, and the cell resistance was read on a five-dial decade resistance box (Muirhead A-25-N), the null point being detected with a Cossor double-beam oscilloscope (Model 1035).

Thermostatic control was maintained by means of a Variac transformer and electrical heater in a well-stirred oil-bath contained in a 5-l. transparent Dewar vessel. Temperatures were measured on mercury thermometers which had been calibrated at 5° intervals against NPL standard thermometers.

## RESULTS

Gallium tribromide was the first compound to be investigated and it was also the one studied in greatest detail. The sublimate in the conductivity cell was momentarily fused and then allowed to solidify as a compact mass around the electrodes. The conductivity of the solid was measured between

[16] J. D. CORBETT and R. H. MCMULLAN *J. Amer. Chem. Soc.* 77, 4217 (1955).
[17] N. N. GREENWOOD, R. L. MARTIN, and H. J. EMELÉUS *J. Chem. Soc.* 3030 (1950).

100° and 121° and then readings were taken on the liquid up to 134°. The results are tabulated as run 1 in Table 1 and are also presented graphically in Fig. 3. It is seen that the conductivity of the solid increases rapidly to a maximum value at a temperature of 115–119° and then, 3° below the m.p., it suddenly drops by a power of 10. The decrease continues throughout the melting process, the conductivity reaching a minimum value some 1·5° above the m.p. Thereafter the conductivity rises more slowly.

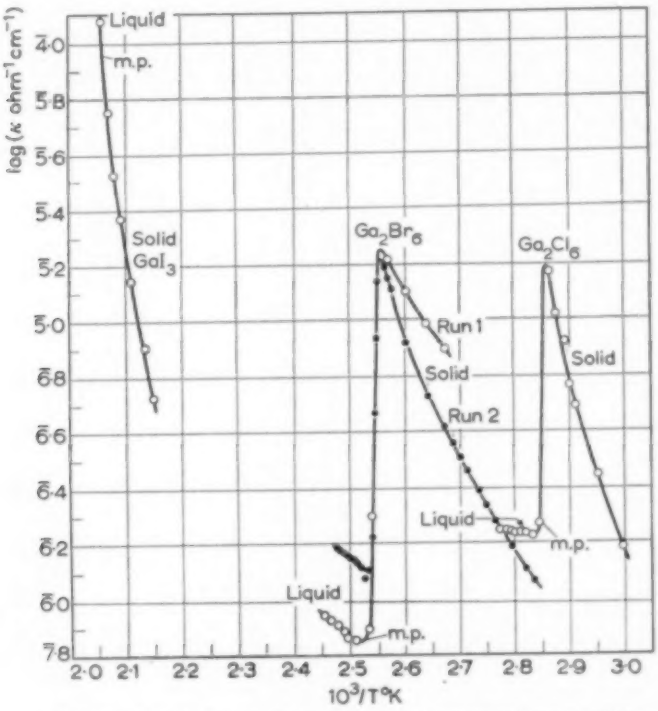


FIG. 3.—Electrical conductivity of solid and molten gallium trihalides.

The temperature was allowed to rise to about 210° over a period of hours, to see if thermal treatment would modify the effect. The run was then repeated by allowing the compound to solidify and cool to 80° before being reheated. It was noted that the conductivity rose sharply with the onset of crystallization as the compound was cooled. The results of the second heating experiment are recorded as run 2 in Table 1 and Fig. 3. It is evident that the effect, though still present, had been decreased in magnitude, presumably due to slight decomposition during the drastic thermal treatment. On this run the decrease in conductivity commenced 6° below the m.p. of the pure compound, but the m.p. of the sample itself at this stage was 1·2° below that of the pure compound. Other experiments carried out on fresh samples of gallium tribromide in different conductivity cells all showed precisely the same type of behaviour.

Gallium trichloride was investigated in the same way. From visual observations of the crystals in the conductivity cell it appeared that, in this case, the drop in conductivity coincided with the onset of melting. The minimum in conductivity occurred 2° above the m.p., after which the conductivity rose very slowly. It proved difficult to get accurately reproducible values for the conductivity of gallium trichloride, but in all experiments the conductivity of the solid was appreciably greater than that of the liquid. A typical set of results is given in Table 2 and is presented graphically in Fig. 3.

TABLE 1.—CONDUCTIVITY OF SOLID AND MOLTEN GALLIUM TRIBROMIDE

| Run 1 | | Run 2 | | | |
|---|---|---|---|---|---|
| $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ | $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ | $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ |
| 100·0 (solid) | 7·895 | 79·1 (solid) | 1·155 | 116·0 (solid) | 15.35 (max.) |
| 105·0 | 9·636 | 81·2 | 1·258 | 117·0 | 13·59 |
| 110·0 | 12·59 | 84·3 | 1·528 | 118·2 | 8·540 |
| 114·8 | 16·45 (max.) | 86·35 | 1·748 | 119·0 | 4·615 |
| 119·7 | 1·992 | 88·2 | 1·907 | 120·0 | 1·696 |
| 121·0 | 0·789 | 90·2 | 2·158 | 121·1 (m.p.) | 1·774 |
| 122·3 (m.p.) | — | 92·0 | 2·430 | 122·0 (liquid) | 1·194 (min) |
| 124·8 (liquid) | 0·717 (min) | 94·4 | 2·838 | 123·0 | 1·316 |
| 127·2 | 0·729 | 96·0 | 3·155 | 124·0 | 1·352 |
| 128·0 | 0·772 | 98·0 | 3·610 | 125·0 | 1·389 |
| 130·0 | 0·812 | 100·2 | 4·138 | 126·0 | 1·413 |
| 132·0 | 0·845 | 105·4 | 5·301 | 127·0 | 1·439 |
| 134·0 | 0·881 | 110·3 | 8·191 | 128·0 | 1·473 |
| | | 114·1 | 12·87 | 129·0 | 1·500 |
| | | 115·0 | 13·89 | 130·0 | 1·528 |

TABLE 2.—CONDUCTIVITY OF SOLID AND MOLTEN GALLIUM TRICHLORIDE

| $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ | $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| 60·5 (solid) | 1·525 | 78·0 (liquid) | 1·864 |
| 65·4 | 2·761 | 79·5 | 1·649 (min) |
| 69·8 | 4·920 | 81·2 | 1·711 |
| 71·1 | 5·791 | 82·2 | 1·727 |
| 72·2 | 8·281 | 83·5 | 1·735 |
| 74·3 | 10·46 | 84·4 | 1·743 |
| 75·6 | 14·76 (max.) | 85·8 | 1·753 |
| 77·75 (m.p.) | — | 87·0 | 1·760 |

TABLE 3.—CONDUCTIVITY OF SOLID AND MOLTEN GALLIUM TRI-IODIDE

| $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ | $t°$ | $10^6 . \kappa$ ohm$^{-1}$ cm$^{-1}$ |
|---|---|---|---|
| 191·8 (solid) | 5·300 | 207·2 | 37·49 |
| 195·1 | 7·991 | 209·0 | 56·16 |
| 200·0 | 13·97 | 211·5 (m.p.) | — |
| 204·2 | 23·29 | 212·0 (liquid) | 118·2 |

The corresponding data for gallium tri-iodide are summarized in Table 3 and Fig. 3. The powdered compound was rapidly fused and solidified before the start of the run, the conductivity of the initial melt being $1·098 \times 10^{-4}$ at 212°. At the m.p. the bright yellow tri-iodide began to

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deepen in colour to brown, and slow decomposition set in with concurrent irreversible increase in conductivity. For this reason the conductivity of the molten compound could not be investigated in detail, but the results indicated that, unlike the other trihalides, gallium tri-iodide showed a slight increase in conductivity during melting.

## DISCUSSION

The points to be discussed are the numerical values of the conductivities, the implied activation energies, and the nature of the structural change occurring near the melting-point.

The conductivities of gallium tribromide and tri-iodide as measured in this work are lower than the values reported by KLEMM and TILK.[12] Their value for the tribromide was $5 \cdot 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ at 124·8°, whereas the present value is $0{\cdot}717 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$. The high value may have been due to some thermal decomposition, since their specimen was heated to 250°; the present results indicate that the conductivity at the melting-point is raised by a factor of 2 after heat treatment at 210°. An alternative explanation is that the earlier results were influenced by the impurities present in the gallium (0·16% In, 0·10% Zn, and less amounts of other elements); these were known to be absent from the present high-purity material (Johnson, Matthey and Co. Ltd.). Similar remarks apply to the tri-iodide for which values of $2 \cdot 10^{-2}$ and $5 \cdot 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ at the m.p. have been quoted[12] on material which was heated as high as 300°. The present results show that, even at 212°, the initial value of $1{\cdot}10 \times 10^{-4}$ increases to $1{\cdot}18 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ within half an hour. This increase was accompanied by a progressive deepening of the colour of the compound, and when part of the cell was allowed to project above the surface of the thermostat bath, iodine sublimed slowly to the cooler parts of the apparatus.

Reproducible results on gallium trichloride were more difficult to obtain, due to large capacity effects in the cell used. However, the value of $1{\cdot}86 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$ quoted in Table 2 for the conductivity of the liquid at the m.p. is probably close to the true value. KLEMM and TILK were unable to obtain a balance point on their apparatus, and concluded that the conductivity was below $10^{-7}$ ohm$^{-1}$ cm$^{-1}$.

From the logarithmic plots of the conductivity against the reciprocal of the absolute temperature, "activation energies" may be computed. For the molten trichloride, the value appears to be 0·9 kcal mole$^{-1}$, and both runs on the tribromide give 6·9 kcal mole$^{-1}$. It is difficult to interpret these figures confidently, because it is by no means evident that the number of ions in the melt just above the m.p. is independent of temperature. Indeed, it is unlikely that this is so, in view of the drastic structural change which the compounds undergo in the region of the m.p. Values for the activation energy in the solid state are less accurate, since these will be influenced by grain-boundary resistances and contact resistances between the sample and the electrodes. Moreover, the graphs are not linear, but increase in slope as the m.p. is approached. For gallium trichloride in the range 60–70° the slope corresponds to 28 kcal mole$^{-1}$, and this increases to nearly 50 kcal mole$^{-1}$ at the m.p. For gallium tribromide, the first run gives values of 12 kcal mole$^{-1}$, increasing to 17 kcal mole$^{-1}$ just below the m.p.; the second run is similar, except for a more rapid increase in slope in the region of the m.p., the final tangent being as high as 27 kcal mole$^{-1}$. The results do suggest, though, that the activation energy for conduction in the solid tribromide is less than that for the solid trichloride. The conductivity of solid gallium tri-iodide increases very rapidly with temperature

and corresponds to an activation energy of 50–60 kcal mole$^{-1}$. The values of these various activitation energies (20–60 kcal mole$^{-1}$) and their increase with temperature are typical of the behaviour of solid ionic conductors.[18]

The phenomenon of an ionic solid melting to give a covalent liquid is already known for phosphorus pentachloride[1, 2, 3, 19] and for aluminium trichloride.[4, 5, 6] To these examples may now be added gallium trichloride, gallium tribromide and, as will be shown, gallium tri-iodide. Phosphorus pentachloride differs from the other four compounds, for, though it has an ionic lattice $PCl_4^+$ $PCl_6^-$, the conductivity of the solid decreases rather than increases with rise in temperature:[19] the conductivity of the solid is $3{\cdot}3 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ at 20° and $3 \cdot 10^{-8}$ ohm$^{-1}$ cm$^{-1}$ at 100°; the conductivity of the liquid at the m.p. (160°) is $6 \cdot 10^{-9}$ ohm$^{-1}$ cm$^{-1}$. It would be instructive to see whether phosphorus pentabromide, which is known to be an ionic solid $PB_4^+$ $Br^-$,[20, 21] shows the same effect, though partial thermal decomposition of the compound below the melting-point may make it difficult to observe.

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The conductivity of solid aluminium trichloride,[5] and of gallium trichloride and tribromide, all increase with rise in temperature and then fall rapidly at, or just below, the m.p. The largest decrease on melting appears to be that of gallium tribromide (twenty-three-fold), the two trichlorides decreasing about ten-fold. Aluminium tribromide and tri-iodide, on the other hand, and also gallium tri-iodide, do not show the effect, but for different reasons. The aluminium compounds are covalent both as solids and as liquids,[5, 22] whereas the conductivity results imply a certain degree of ionization in both the solid and the molten gallium tri-iodide. However, as the conductivity of a fully ionized ionic compound normally increases by a factor of $10^2$–$10^3$ on melting, the fact that the conductivity of gallium tri-iodide is of the same order of magnitude in both phases may still be taken to imply a large decrease in the number of ions on melting, the conductivity remaining at about the same value because of the greatly increased mobility of the smaller number of ions. Thus the conductivity of solid gallium tri-iodide just below its m.p. is similar in magnitude to that of an ionic compound such as sodium chloride,[23] but the conductivity of the molten tri-iodide is less than that of molten sodium chloride[24] by a factor of $10^4$ even when molar conductivities rather than specific conductivities are compared. Since the viscosities of the two compounds are about the same, the comparison implies that the degree of ionic dissociation of molten gallium tri-iodide is less than 1% and possibly as low as $10^{-2}$%. In short, conductivity results on all three trihalides of gallium may be interpreted as indicating a drastic reduction of the number of ions in the region of the m.p., the ionic solids giving rise to covalent molecular liquids, which are but slightly ionized.

The considerable electrical conductivity of solid gallium trichloride suggests that the interpretation of the Raman spectrum of this compound in the solid state[25] may be in error. From a detailed analysis of the spectrum of the molten compound and the general similarity in spectra of the solid and liquid states, it was concluded

[18] N. F. Mott and R. W. Gurney *Electronic Processes in Ionic Crystals* Oxford University Press, 1940.
[19] J. H. Simmons and G. Jessop *J. Amer. Chem. Soc.* **53**, 1263 (1931).
[20] H. M. Powell and D. Clark *Nature* **145**, 971 (1940).
[21] M. von Driel and C. H. MacGillavry *Rec. trav. chim.* **62**, 167 (1943).
[22] P. A. Renes and C. H. MacGillavry *Rec. trav. chim.* **64**, 275 (1945).
[23] A. Smekal *Handb. der Phys.* **24**/2, 881 (1933).
[24] W. Biltz and W. Klemm *Z. anorg. Chem.* **152**, 267 (1926).
[25] H. Gerding, H. G. Haring, and P. A. Renes *Rec. trav. chim.* **72**, 78 (1953).

that the dimeric molecular structure persisted when the compound crystallized. It is relevant that a similar error was made in the interpretation of the Raman spectrum of solid aluminium trichloride: this was considered to indicate the presence of dimeric molecules by analogy with the spectrum of the molten compound,[6] whereas a later X-ray structure determination[26] showed that the solid was, in fact, ionic, in agreement with the conductivity results.[5] For this reason a complete X-ray structure analysis of gallium trichloride and tribromide is at present being carried out in this laboratory.

From the foregoing remarks it is clear that the energy balance between ionic and covalent forms of certain halides is delicately poised, and it is of interest to speculate on the existence of other highly conducting ionic solids which might melt to give poorly conducting molecular liquids. Phosphorus pentabromide has already been mentioned. The tri-iodides of arsenic, antimony, and bismuth also have ionic lattices, the metal ion being octahedrally surrounded by six iodide ions, yet the compounds are low-melting and form pyramidal molecules at least in the gas phase.[27] Ferric chloride is another possible example, since it is a low-melting ionic solid which nevertheless exists as dimeric molecules $Fe_2Cl_6$ in the vapour phase.[27] Indeed, the phenomena may be far more widespread than the four or five examples which are known at present would indicate, since the many oxidation states of the transition elements alone, with their gradation from ionic to covalent properties, coupled with the known effect of the halogens in modifying ionic properties, provide numerous examples of such borderline compounds which would repay further structural and electrochemical investigation both in the solid and in the liquid phase.

The effect is unlikely to be confined to halides alone: for example, dinitrogen pentoxide may well be found to melt with a substantial decrease in electrical conductivity. The solid is ionic, $NO_2^+NO_3^-$,[28] yet its volatility and low m.p. (41° under pressure) suggest that the ionic form readily passes over into the covalent, molecular configuration $O_2N—O—NO_2$. In this instance, however, there would be considerable experimental difficulty in measuring the conductivity because of the rapid thermal decomposition of the compound and its tendency to explode spontaneously.

*Note Added in Proof*—Dinitrogen tetroxide has very recently been shown to have a higher conductivity in the solid than in the liquid phase.[29] The conductivity of the supercooled liquid at −20° is $5{\cdot}4 \times 10^{-14}$ ohm$^{-1}$cm$^{-1}$; that of the polycrystalline solid is about 1000 times greater.

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[26] J. A. A. KETELAAR, C. H. MACGILLAVRY, and P. A. RENES *Rec. trav. chim.* **66**, 502 (1947).
[27] A. F. WELLS *Structural Inorganic Chemistry* 2nd Ed. Oxford University Press, 1950.
[28] E. GRISON, K. ERIKS, and J. L. DE VRIES *Acta Cryst.* **3**, 290 (1950).
[29] R. S. BRADLEY *Trans. Faraday Soc.* **52**, 1255 (1956).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 365 to 366. Pergamon Press Ltd., London

# THE PREPARATION OF RHODIUM(III) PERCHLORATE HEXAHYDRATE

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**Abstract**—A stable rhodium(III) perchlorate hexahydrate, $Rh(ClO_4)_3 \cdot 6H_2O$, has been prepared by reaction of perchloric acid with rhodium(III) chloride. The compound is crystalline and water-soluble. X-ray powder diffraction data are given.

## INTRODUCTION

AMONG the numerous rhodium compounds reported in the literature, the only reference to a perchlorate of rhodium was found in papers by GRUBE *et al.* In an investigation of the electrolytic separation of rhodium, GRUBE and KESTING[2] prepared "rhodium perchlorate" by dissolving freshly precipitated rhodium(III) hydroxide in one-third of the indicated molar quantity of perchloric acid; these authors postulated a solution complex of the composition $Rh(OH)_2^+$. GRUBE and AUTENRIETH[3] investigated higher oxidation states of rhodium by following anodic oxidation of rhodium(III) solutions; their paper refers to the dissolution of $Rh(OH)_2ClO_4$, prepared by crystallization from rhodium(III) hydroxide and perchloric acid solutions.

During an investigation in this laboratory of the solution chemistry of rhodium(III) and its higher oxidation states, it was desirable to minimize the complexation of the rhodium ion; for this reason, the preparation of rhodium(III) perchlorate was undertaken. Working with concentrated perchloric acid solutions, it was possible to isolate a salt of the composition $Rh(ClO_4)_3 \cdot 6H_2O$. This compound is water-soluble and crystalline. Its extreme hygroscopic character necessitates isolation under anhydrous conditions.

The X-ray powder data can be indexed on the basis of a face centered cubic structure with a unit cell of 11·16 Å $\pm$ 0·02 Å. This suggests that the compound has the $(NH_4)_3FeF_6$ structure;[4] the compounds $Co(ClO_4)_3 \cdot 6NH_3$, $Co(ClO_4)_3 \cdot 5NH_3 \cdot H_2O$, $Cr(ClO_4)_3 \cdot 6NH_3$, and $Cr(ClO_4)_3 \cdot 5NH_3 \cdot H_2O$ also have this structure.[5] A reasonable structure can be formulated by assuming coordination of the water to the rhodium(III) cation. Experiments have shown that replacement of water may easily be made with other ligands.*

## EXPERIMENTAL

### *Materials and method.*

Rhodium(III) chloride tetrahydrate obtained from A. D. Mackay, Inc., was examined spectrographically and found to be of purity greater than 99·7%. Approximately two grams of this compound were dissolved in 25 ml. of water; 30 ml. of perchloric acid (72%) and several boiling beads were added, and the mixture was evaporated to a volume of 25 ml. A red-brown precipitate (possibly a

* Drying of the dioxane substituted product resulted in its violent decomposition.

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[2] G. GRUBE and E. KESTING *Z. Elektrochem.* **39**, 955 (1933).

[3] G. GRUBE and H. AUTENRIETH *ibid.* **44**, 296 (1938).

[4] L. PAULING *J. Amer. Chem. Soc.* **46**, 2738 (1924).

[5] R. W. G. WYCKOFF *Crystal Structures* Vol. II, Chap. X, Table XF, 11, Interscience Publishers, New York (1951).

chloro-perchlorate) appeared during this procedure, but further boiling resulted in complete re-dissolution of the precipitate. The mixture was cooled, 10 ml more perchloric acid were added, and fuming was continued to a final volume of 10 to 15 ml. The solution was allowed to cool to room temperature; the rhodium perchlorate separated in the form of needles 0·5 to 1 mm in length. The crystals were transferred rapidly to a medium-porosity filtering crucible modified at each end for sealing. The crystals were washed immediately with recently boiled, cold perchloric acid. When the wash liquid was a constant light yellow colour, the filter was transferred to a vacuum drying chamber. The compound was dried at 110°C and a pressure of about $10^{-3}$ mm of mercury, then sealed in the filter capsule until ready for use. The rhodium perchlorate hydrate consisted of light yellow, fluffy needles. Darkening of colour occurred whenever completely anhydrous conditions were not observed.

### *Analysis*

The rhodium content was determined by reduction with hydrogen at 500°C, and also by the spectrophotometric method of AYRES and YOUNG.[6] Perchlorate was determined gravimetrically with nitron.[7] Methods utilizing the reduction of perchlorate to chloride were excluded due to the difficulty of determining chloride in the presence of rhodium. Water was determined by the usual semimicro method. Calculated for $Rh(ClO_4)_3 \cdot 6H_2O$: Rh, 20·2%; $ClO_4$, 58·7%; $H_2O$, 21·1%. Found: Rh, 20·2%; $ClO_4$, 58·1%; $H_2O$, 21·6%.

### *X-ray powder pattern*

Powder patterns were recorded for the needles obtained as described above, as well as from large crystals obtained by slow evaporation of a concentrated solution; identical patterns were obtained from the two materials. The principal lines are given in Table 1.

TABLE 1.—PRINCIPAL X-RAY DIFFRACTION LINES FOR $Rh(ClO_4)_3 \cdot 6H_2O$

| *hkl* | *d*, Å, calcd. | *d*, Å, obsvd. | $I/I_1$ |
|---|---|---|---|
| 111 | 6·44 | 6·46 | 24 |
| 200 | 5·58 | 5·60 | 21 |
| 220 | 3·95 | 3·94 | 100 |
| 311 | 3·36 | 3·36 | 10 |
| 400 | 2·79 | 2·79 | 36 |
| 420 | 2·50 | 2·49 | 9 |
| 422 | 2·28 | 2·28 | 16 |
| 511, 333 | 2·15 | 2·15 | 24 |
| 440 | 1·98 | 1·97 | 10 |
| 531 | 1·89 | 1·89 | 10 |
| 600, 442 | 1·86 | 1·86 | 10 |
| 620 | 1·76 | 1·76 | 14 |
| 711, 551 | 1·56 | 1·56 | 9 |
| 642 | 1·49 | 1·49 | 14 |
| 822, 660 | 1·32 | 1·31 | 3 |

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[6] G. H. AYRES and F. YOUNG *Analyt. Chem.* **24**, 165 (1952).
[7] O. LOEBICH *Z. anal. Chem.* **68**, 34 (1926).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 367 to 369. Pergamon Press Ltd., London

# QUINQUEVALENT COMPOUNDS OF URANIUM—I ALKOXIDES AND COMPLEX CHLORIDES

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**Abstract**—The new complex, $(C_5H_6N)_2UOCl_5$ (I), was obtained from reactions involving $UCl_5$, $SOCl_2$, alcoholic hydrogen chloride, and pyridine. Reaction of (I) with alcohol and ammonia afforded a novel method of preparing uranium penta-alkoxides $U(OR)_5$ by disproportionation of the oxide-alkoxides initially formed. The new compound, $UOCl_3$,EtOH(II), was isolated from the reaction involving $UCl_5$,$SOCl_2$ and very dry ethyl alcohol, and this explains the formation of (I).

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OUR knowledge of quinquevalent uranium appears to be limited to the facts that some moderately stable solids $UF_5$ and $UCl_5$[1] exist whilst in solution[2] the unstable ion $UO_2^+$ rapidly disproportionates into the quadrivalent ($U^{4+}$) and sexivalent ($UO_2^{2+}$) ions. In addition, uranium oxytrichloride $UOCl_3$ has been claimed as an intermediate product in the chlorination of uranium trioxide using carbon tetrachloride,[3] and HECHT *et al.*[4] obtained the complex $UCl_5$,$SOCl_2$ by chlorination of the trioxide with thionyl chloride.

The pentachloride-thionyl chloride complex seemed a promising starting material for the preparation of uranium penta-alkoxides, and our initial aim was the preparation of a quinquevalent pyridinium complex such as $(C_5H_6N)UCl_6$ which would then be treated with alcohol and ammonia. However, treatment of the alcoholic solution of $UCl_5$, $SOCl_2$ with pyridine gave the complex oxychloride $(C_5H_6N)_2UOCl_5$(I). The U-O grouping is evidently formed in the initial reaction between the pentachloride-thionyl chloride complex and the alcohol, because the new oxytrichloride alcoholate $UOCl_3$, EtOH(II) was isolated from this system in spite of the precaution of using very dry ethanol. The alcoholate (II) was insoluble in benzene, but its molecular weight was determined ebullioscopically in ethanol. A dimeric molecule involving 6-co-ordinate uranium was expected, but the apparent molecular complexity was 0·84. If it is assumed that the uranium has a co-ordination number of 6, it then follows that the compound is further solvated and possibly ionized in boiling ethanol:—

$$UOCl_3,EtOH\ (solid) + EtOH \rightleftharpoons UOCl_3,2EtOH\ (soln.)$$

$$UOCl_3,2EtOH + EtOH \rightleftharpoons [UOCl_2,3EtOH]^+ + Cl^-$$

The formula $(C_5H_6N)_2U^{V}OCl_5$ for compound (I) was supported by analytical experiments, although they do not distinguish between the possibilities of a quinquevalent compound or a mixed quadrivalent-sexivalent compound. A preliminary

[1] J. J. KATZ and E. RABINOWITCH The Chemistry of Uranium, pp. 398 and 488 *N.N.E.S.*, Vol. VIII-5, McGraw-Hill, New York (1951).
[2] M. W. LISTER *Quart. Reviews* **4**, 22 (1950).
[3] J. J. KATZ and E. RABINOWITCH The Chemistry of Uranium, p. 492, *N.N.E.S.* Vol. VIII-5, McGraw-Hill, New York (1951).
[4] H. HECHT, G. JANDER, and H. SCHLAPMANN *Z. anorg. Chem.* **254**, 255 (1947).

investigation of the absorption spectra of the aqueous solution of (I) confirmed the presence of quadrivalent and sexivalent uranium into which this quinquevalent compound would be expected to disproportionate. The complex (I) was unchanged by prolonged heating at 120–140° C *in vacuo*, and is thus a comparatively stable quinquevalent uranium compound, since the binary halides $UF_5$ and $UCl_5$ tend to dissociate and/or disproportionate when heated. The quinquevalent formulation of (I) was reinforced by its behaviour with alcoholic ammonia. When either ethanol or isopropanol was used, the corresponding uranium oxide-alkoxide apparently was formed and then converted by thermal disproportionation without change of valency into the uranium penta-alkoxide.

e.g. $(C_5H_6N)_2UOCl_5 + 5NH_3 + 3ROH \rightarrow OU(OR)_3 + 5NH_4Cl + 2C_5H_5N$

$$nUO(OR)_3 \rightarrow U(OR)_5 + U_{n-1}O_n(OR)_{3n-5}$$

Uranium pentaethoxide was a brown mobile liquid, as described by TAYLOR *et al.*,[5] who prepared the compound by a different method. The penta-isopropoxide, a new compound, was a golden crystalline solid which was crystallized unchanged from isopropanol. These penta-alkoxides are very susceptible to hydrolysis and to oxidation by air, but they seem surprisingly resistant to valency disproportionation, since they can be distilled unchanged under reduced pressure. Work now in progress shows that the hexaethoxide $U(OEt)_6$ is more volatile than $U(OEt)_5$ and the tetraethoxide would be expected to be considerably less volatile, so that thermal valency disproportionation should be detected by the procedure of vacuum distillation. The complex (I) appears to be the first recorded example of a compound containing the complex quinquevalent ion $[UOCl_5]^{2-}$, and this has a formal analogy to the quinquevalent complexes of chromium,[6] molybdenum,[7] and tungsten.[8] However, it cannot yet be ruled out that the uranium compound may contain two types of anion $[UCl_4]^{2-}$ and $[UO_2Cl_4]^{2-}$, both of which are well established. It is hoped that X-ray diffraction and other physical studies now in progress will settle the constitution of (I).

## EXPERIMENTAL

The apparatus and experimental technique used in this work were similar to that which has already been described.[9]

*Analysis.* Uranium was precipitated as the ammonium diuranate (after oxidation with dil. nitric acid) and ignited to $U_3O_8$. Chloride was determined gravimetrically on the filtrate from the uranium determination. The valency of uranium in (I) was established by two volumetric methods. In one the chloride was first precipitated by addition of the exact amount of silver sulphate in dilute sulphuric acid solution. The filtrate was then titrated with standard permanganate (to determine the $U^{4+}$ concentration) and then passed through the Jones reductor, aerated for 5 mins, and titrated again to determine total uranium (as $U^{4+}$). In the second method, the quadrivalent uranium was determined by the addition of an excess of standard ceric sulphate solution followed by backtitration with ferrous ammonium sulphate. Total uranium was determined on a separate sample by the same procedure, following the complete reduction to $U^{4+}$ by the reductor method. In the case of the alkoxides, the "apparent" total uranium determined by method (I) was higher than that found gravimetrically. This was shown to be due to oxidation of the liberated alcohol by permanganate, catalysed by $U^{4+}$. Further research proved that the *ratio* of the initial titration to the total uranium titration gave a true index of the proportion of $U^{4+}$ in the compound. The ethoxide and isopropoxide determinations

[5] T. I. TAYLOR, E. R. SMITH, J. L. JORGENSEN, H. MATHESEN, and J. K. TAYLOR *A.E.C.D.* 3144.
[6] R. F. WEINLAND *et al.*, *Ber.* **38**, 3784 (1905); **39**, 4042 (1906); **40**, 2090 (1907).
[7] W. WARDLAW *et al. J. Chem. Soc.* 2145 (1927); 2726 and 2742 (1928); 2578 (1929).
[8] O. COLLENBERG and A. GUTHE *Z. anorg. Chem.* **134**, 322 (1924).

were made by the chromic-acid method,[9] with due allowance for the oxidation of $U^{V}$ to $U^{VI}$. The carbon, hydrogen, and nitrogen analyses were carried out at the Microanalytical Laboratory, Imperial College of Science.

### *Preparation of* $UCl_5,SOCl_2$

The sealed-tube technique of HECHT (loc. cit.) was not suitable on the large scale, but we have found that the reaction takes place slowly under normal reflux, with an excess of thionyl chloride. Uranium trioxide (25 g) was added to thionyl chloride (700 c.c.) and the system maintained under reflux for 14 days. The thionyl chloride was then removed by normal distillation to small bulk, followed by final evaporation under reduced pressure, and gave a brown crystalline product (46 g). Found: U 44·9, Cl 44·2. Calc. for $UCl_5,SOCl_2$: U 44·6, Cl 46·5%.

### *Preparation of* $UOC_3,EtOH$.

Addition of ethanol (30 c.c., water content <0·005%) to the pentachloride-thionyl chloride complex (2·5 g) caused a vigorous exothermic reaction. After sulphurous impurities had been filtered off, the deep green solution was evaporated to dryness at 70°C under 0·05-mm pressure and gave a dark brown powder. Found: U 58·8, Cl 26·1, OEt 13·2. $UOCl_3,EtOH$ requires: U 58·6, Cl 26·2, OEt 11·1%. Mol. wt.: Found, 340; $UOCl_3,EtOH$ requires: 406·5.

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### *Preparation of* $(C_5H_6N)_2\ UOCl_5$

The complex $UCl_5$, $SOCl_2$ (22 g) was allowed to react with ethanol (400 c.c.), and the solution after filtration was saturated with anhydrous hydrogen chloride. Pyridine (12 g) was then added, and the pale green crystalline complex (26 g) was filtered off and dried under reduced pressure. Found: U (grav.) 40·0 U (vol.) 40·1, $U^{IV}$ (vol.) 19·9, Cl 31·1, C 20·4, H 2·2, N 4·7. $(C_5H_6N)_2\ UOCl_5$ requires: U 40·2, $U^{IV}$ 20·1, Cl 30·0, C 20·3, H 2·0, N 4·7%.

### *Preparation of uranium pentaethoxide*

The pyridinium complex (24 g), previously dried at 140°C/0·1 mm, was suspended in a mixture of benzene (500 c.c.) and ethanol (60 g) and treated with anhydrous ammonia. When the exothermic reaction was complete, the ammonium chloride was filtered off and the filtrate was evaporated to dryness under reduced pressure. The final product after drying for 2 hr at 80°C/0·05 mm was a brown gum (14 g; theory for $UO(OEt)_3$, 16 g). Found: U (grav) 61·7, $U^{IV}$ (vol.) 30·0, OEt 34·1. $UO(OEt)_3$ requires: U 61·2, $U^{IV}$ 30·6, OEt 34·7%. The uranium oxide triethoxide when heated at 140–160°C/0·05 mm gave a volatile mobile brown distillate (4 g). Found: U (grav.) 51·0, $U^{IV}$ (vol.) 26·2, OEt 48·8. $U(OEt)_5$ requires: U 51·4, $U^{IV}$ 25·7, OEt 48·6%. The residue from the distillation is being further examined.

### *Preparation of uranium penta-isopropoxide*

The pyridinium complex (9 g) suspended in benzene (70 c.c.) and isopropanol (50 c.c.) was treated with ammonia. After the removal of ammonium chloride and solvent as before, a light brown solid was obtained. This was heated at 150°C/0·05 mm in a molecular still and gave a golden crystalline sublimate of the penta-isopropoxide which was crystallized unchanged from isopropanol. Found: U (grav.) 44·7, $U^{IV}$ (vol.) 21·5, $OPr^{i}$ 53·8. $U(OPr^{i})_5$ requires: U 44·6, $U^{IV}$ 22·3, $OPr^{i}$ 55·4%.

The authors are indebted to Prof. W. WARDLAW, C.B.E., for his interest and encouragement during this work.

[9] D. C. BRADLEY A. K. CHATTERJEE, and W. WARDLAW *J. Chem. Soc.* 2260 (1956).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 370 to 378. Pergamon Press Ltd., London

# THE MUTUAL SEPARATION OF THORIUM, PROTOACTINIUM, AND URANIUM BY TRIBUTYL PHOSPHATE EXTRACTION FROM HYDROCHLORIC ACID*

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**Abstract**—The distribution behaviour of U(VI) and Pa(V) in the system aqueous HCl—TBP (tributyl phosphate) without diluent has been investigated at 22 ± 2°C and the results compared with those reported for Th(IV) in the same system. From the comparison, it is postulated that protoactinium extracts respectively as oxygenated and nonoxygenated entities in the regions of low and high concentration of HCl, the transition range being 4–5 M HCl in the aqueous phase.

Although the data indicate the feasibility of mutual separation of Th(IV), Pa(V), and U(VI) in the HCl—TBP system, the separation of Pa(V) from U(VI) is much more readily achieved in the (HCl, HF)—TBP system; since the complexing action of fluoride ion is much more pronounced for Pa(V) than for U(VI), under the conditions investigated.

A protoactinium sample stored in the form of an (HCl, HF) aqueous solution in a polyethylene container for five years exhibited reversible behaviour, the protoactinium extracting into TBP following addition of boric acid to destroy the fluoride complex. There was no evidence of deposition of protoactinium on the walls of the container.

Equilibrium was attained rapidly in all protoactinium extractions in which no "nonextractable" protoactinium was involved. The "nonextractable" form converts slowly to the "extractable" form in the presence of hydrochloric acid. The rate of this conversion increases with increasing acid concentration and with increasing temperature.

The mutual separation of Th(IV), Pa(V), and U(VI) has been demonstrated for both synthetic and "natural" feeds.

## INTRODUCTION

IN the program of isolation of gram quantities of $Th^{230}$ (ionium) from a pitchblende concentrate, reported elsewhere,[1] one of the collateral problems was the investigation of this concentrate as a likely source of $Pa^{231}$. The aqueous supernate from a fluoride-precipitation step in the ionium-isolation process, having an average $Pa^{231}$ content of 0·3 mg per litre,[1] was processed for $Pa^{231}$ by use of a series of extractive techniques.[2]

With the dual purpose of increasing the yield of $Pa^{231}$ from this ionium-process waste and devising a procedure for the isolation of $Pa^{231}$, plus accompanying $Pa^{233}$, from a neutron-irradiated ionium source,[3] an investigation of the comparative solvent extraction behaviour of Th, Pa, and U was undertaken. (A neutron-irradiated ionium sample contains $Pa^{231}$ and $Pa^{233}$ formed respectively from $Th^{230}$ and $Th^{232}$ through neutron capture, $U^{232}$ formed from $Pa^{231}$ through secondary neutron capture, $U^{233}$ formed from $Pa^{233}$ through beta decay, and the daughters of $U^{232}$.)

* Based on work performed under the auspices of the US Atomic Energy Commission and reported, in large part, in Argonne National Laboratory Report ANL-4490, pp. 62–74, (April–June 1950).

[1] D. F. PEPPARD, G. ASANOVICH, R. W. ATTEBERRY, O. DUTEMPLE, M. V. GERGEL, A. W. GNAEDINGER, G. W. MASON, V. H. MESCHKE, E. S. NACHTMAN, and I. O. WINSCH *J. Amer. Chem. Soc.* **75**, 4576 (1953).

[2] R. ELSON, G. W. MASON, D. F. PEPPARD, P. A. SELLERS, and M. H. STUDIER *J. Amer. Chem. Soc.* **73**, 4974 (1951).

[3] The transmutation of $Th^{230}$ to $Pa^{231}$ through neutron irradiation has been demonstrated by E. K. HYDE, Argonne National Laboratory Report *ANL*-4183 (Aug. 1943).

The conditions of high yield and high degree of purity of protoactinium product having been imposed, a preliminary evaluation was made during which several otherwise-promising systems were discarded because of the difficulty in obtaining reproducible protoactinium behaviour. Since this difficulty, possibly due to hydrolytic phenomena,[2] was minimal in systems involving hydrochloric acid, the detailed

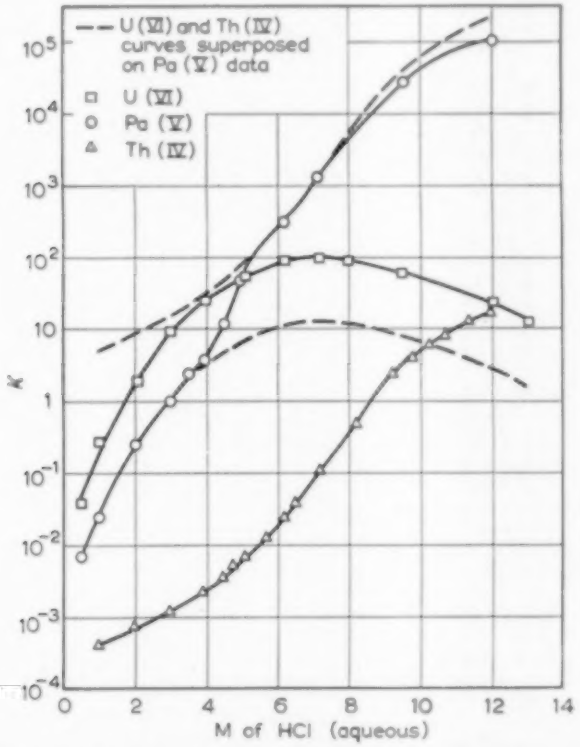


FIG. 1—Variation of distribution ratio of U(VI), Pa(V), and Th(IV) with aqueous HCl concentration using TBP without diluent. The Th data are from PEPPARD, MASON and MAIER.[6]

investigation was restricted to aqueous phases which contained HCl[4] or HCl plus HF.[5] The study presently reported involved these aqueous phases and tri-*n*-butyl orthophosphate, $(n\text{-}C_4H_9O)_3PO$, symbolized as TBP, without diluent, as the opposing phase. Data pertaining to the behaviour of Th(IV), Pa(V), and U(VI) in these systems are presented, and the mutual separation of this sequential triad is demonstrated. The Th data of Fig. 1 have been reported by PEPPARD, MASON, and MAIER.[6]

[4] The extractability of protoactinium into organic solvents from aqueous phases containing inorganic chloride salts or hydrochloric acid or mixtures of these solutes is reported by: (a) A. G. MADDOCK and L. H. STEIN *J. Chem. Soc.* Suppl. No. 2, 258 (1949); (b) K. A. KRAUS and G. E. MOORE *J. Amer. Chem. Soc.* **72**, 4293 (1950); (c) R. ELSON *et al.*[2] and (d) F. L. MOORE *Analyt. Chem.* **27**, 70 (1955).

[5] The use of HF for decreasing the liquid-extraction distribution ratio of protoactinium by complexing it in an aqueous phase is reported by (a) ELSON *et al.*[2] (b) MOORE,[4d] and (c) J. GOLDEN and A. G. MADDOCK *J. Inorg. Nucl. Chem.* **2**, 46 (1956).

[6] D. F. PEPPARD, G. W. MASON, and J. L. MAIER, accepted for publication in *J. Inorg. Nucl. Chem.*

## EXPERIMENTAL

Tributyl phosphate, purchased from Commercial Solvents Corporation, was prepared for use by the procedure reported by PEPPARD, MASON, and MAIER.[6] Diisopropyl ketone was obtained from Eastman Kodak Co. and used as received. The alpha-active nuclides $8{\cdot}0 \times 10^4$-*y* $Th^{230}$, $3{\cdot}4 \times 10^4$-*y* $Pa^{231}$, and $1{\cdot}6 \times 10^5$-*y* $U^{233}$ were obtained from the Argonne National Laboratory's stocks. Each of these nuclides was shown to be free from alpha-active contaminants other than isotopic ones.[7] The ionium had a $Th^{232}$ : $Th^{230}$ ratio of approximately 11. Beta-active 27·4-*d* $Pa^{233}$ was obtained from M. H. STUDIER of A.N.L.

The distribution ratio, *K* (concentration in the TBP, upper, phase divided by concentration in the aqueous, lower, phase at equilibrium) was determined as in previous studies in the series.[8] In each case, the *K* value was confirmed by approaching the assumed equilibrium from both sides as follows. An aqueous phase containing the radioactive nuclide was equilibrated against the initially barren (with respect to the radioactive nuclide) TBP. Following removal of aliquots of the separated phases for analysis, the TBP extract was equilibrated against a barren aqueous scrub initially identical in composition to the first aqueous phase except that it contained none of the nuclide under investigation. Aliquots of the equilibrated phases were taken for analysis. In each determination, the volumes of upper and lower phases were identical. The TBP solvent was, in each case, pre-equilibrated by equilibrating it against at least four triple-volume portions of the aqueous acid to be used. The possibility of complicating polymerizations was ruled out by demonstrating the essential constancy of *K* over a fifty-fold or larger range of concentrations of tracer-level solute. All equilibrations were of 3-minute duration. All data were obtained at $22 \pm 2$°C. Within this four-degree range, no temperature effect was noted. Except as otherwise noted, glass equipment was used.

Most of the Pa data of Fig. 1 and Table 1 were obtained for $Pa^{231}$, since in the determination of *K* values in the very high or very-low-range alpha counting is to be preferred to beta counting. However, checks made at 2·0, 3·96, 4·5, 6·20, and 7·2 M HCl yielded statistically identical data for $Pa^{233}$ and $Pa^{231}$, despite the fact that the molar concentration of Pa differed by a factor approximating to $10^5$.

TABLE 1.—EXTRACTION OF Pa(V) AND U(VI) INTO TBP FROM AQUEOUS HCl AND AQUEOUS HCl, HF PHASES

| Equil. aqueous phase | *K* | |
|---|---|---|
| | Pa(V) | U(VI) |
| 5·0 M HCl | 41·0 | 50·2 |
| 5·0 M HCl, 0·5 M HF | 0·13 | 39·3 |
| 4·0 M HCl | 3·7 | 25·2 |
| 4·0 M HCl, 1·0 M HF | — | 10·4 |
| 0·5 M HCl | — | 0·040 |
| 0·5 M HCl, 1·0 M HF | — | 0·0076 |

In all determinations of *K* values for Pa nuclides, the aqueous feed was prepared by heating the Pa in aqueous 5 to 12 M HCl at 60°C for 3 to 16 hours, extracting the Pa at $22 \pm 2$°C from this aqueous phase into pre-equilibrated TBP, scrubbing the TBP extract with two equal-volume portions of HCl of the same concentration as the original aqueous phase, and re-extracting a sufficient portion of the Pa into aqueous HCl for the desired determinations.

These HCl re-extracts were then, in general, used for *K* determinations within a 4-hour period. Such re-extracts, immediately made 7 to 9 M in HCl and scrubbed with benzene to remove traces

[7] The distribution of energies of the alpha particles, used in identifying certain nuclides and establishing the purity of a sample, was determined by J. F. MECH using the multichannel differential pulse analyser described by A. GHIORSO, A. H. JAFFEY, H. P. ROBINSON and B. B. WEISSBOURD *The Transuranium Elements* McGraw-Hill Book Co., New York, N.Y. (1949). National Nuclear Energy Series, Plutonium Project Record Vol. 14B, Div. IV, Paper 16.8 (1949).

[8] D. F. PEPPARD, J. P. FARIS, P. R. GRAY, and G. W. MASON *J. Phys. Chem.* **57**, 294 (1953).

of TBP, have been used as feed sources for 2-week periods with less than 5% reversion of the Pa to the "nonextractable" form. It is apparent that the effect of such reversion is negligible on determinations of low $K$ values but important in determination of high $K$ values. Consequently, all of the latter determinations were made on freshly-prepared feeds.

The nonextractable entity converts to an extractable one in aqueous 4 to 13·3 M HCl media. The rate of conversion increases with increasing acid concentration and with increasing temperature.

In all determinations of $K$ values for Pa nuclides in which equilibrium was approached from the opposite direction, a barren aqueous phase was equilibrated against a TBP extract within a 1-hour period following the preparation of the latter. However, a TBP extract formed by equilibration against a 5 M HCl aqueous phase showed reproducible Pa behaviour for a 5-hour period. (In such extracts, a phenomenon more important than the possible formation of "nonextractable" Pa is the formation of dibutyl hydrogen phosphate through acid hydrolysis of TBP, since even a small concentration of this compound will greatly enhance the measured $K$ values. The rate of such solvent hydrolysis increases with increasing acid concentration.)

In obtaining the Th and U data, no especial precautions were necessary other than preventing the formation of TBP hydrolysis products.

In the mutual separation of Th, Pa, and U, the technique used was that entitled "countercurrent distribution" by CRAIG.[9] Specifically, each separate portion of TBP remained in its given contactor in which it was equilibrated successively with separate portions of the aqueous phase, each of which was, in turn, transferred to the next successive contactor. In each separation, a single portion of aqueous feed was followed by multiple portions of aqueous scrub. Consequently, if the first aqueous phase effluent from the terminal contactor is considered to be the first product phase, and all other aqueous phases effluent from the terminal contactor are numbered successively, a plot of solute content vs. product number will give a CRAIG[9] plot which bears a close resemblance to ion-exchange elution curves.[10] In all of the figures, each of the aqueous phases is considered, for plotting purposes only, to have the same concentration of hydrochloric acid upon leaving the terminal contactor as upon entering the initial contactor. (It is obvious that, in actuality, the first U products have HCl contents far greater than those of the succeeding products.)

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## RESULTS

Each of the data of Fig. 1 and Table 1 represents the average of at least four determinations, equally divided between the two directions of approach to equilibrium. No result differed from the average by more than one-hundred parts per thousand. Experiments performed with 5 M HCl—TBP showed that equilibrium was attained, from either direction, in a 30-sec period of violent agitation. However, since such efficient agitation is difficult to produce under operating conditions, a standard 3-min period of agitation was adopted.

The distribution ratio data of Fig. 1 and Table 1 show the chemical feasibility of a mutual Th, Pa, U separation. From Fig. 1 it is apparent that both Pa(V) and U(VI) may be preferentially extracted into TBP from 5 M HCl leaving Th(IV) predominately in the aqueous phase.

It is also apparent that at either high- or low-acid concentration the Pa and U $K$-values differ sufficiently to permit mutual separation, in principle. In practice, however, in the low-acid range, Pa hydrolysis difficulties are experienced, and in the high-acid range an awkwardly small volume ratio, $R$, of TBP to aqueous phase is required to make the effective distribution ratio, $RK$, of uranium less than unity.

By reference to Table 1 it is seen that both of these difficulties may be avoided by use of an aqueous phase containing both HCl and HF, the $K$ for U being approximately 300 times that for Pa from a 5 M HCl + 0·5 M HF aqueous phase. It is also

[9] L. C. CRAIG *Analyt. Chem.* **21**, 85 (1949).
[10] See K. A. KRAUS and G. E. MOORE *J. Amer. Chem. Soc.* **77**, 1383 (1955) for curves showing the HCl and the HCl plus HF elution of Pa(V) from a Dowex-1 resin.

apparent from Fig. 1 and Table 1 that U may be re-extracted from a TBP phase into either a 0·5 M HCl or 0·5 M HCl + 1 M HF aqueous phase.

By reference to the HCl distribution data of PEPPARD, MASON, and MAIER,[6] it may be seen that a volume V of aqueous scrub initially 0·5 M in HCl and 1·0 M in HF, following immediately after an equilibrium 5 M HCl scrub in a four-stage system, each stage of which contains a volume V of TBP, will upon exit from the system be approximately 4 M in HCl. For a corresponding three-stage system, the exit

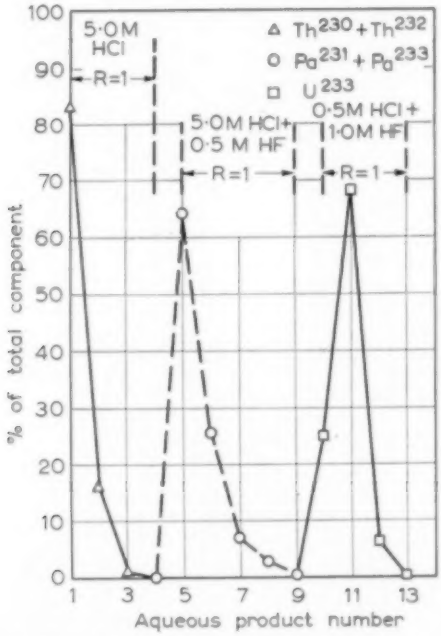


FIG. 2—Mutual separation of Th, Pa, and U from a synthetic feed.
(Three glass contactors used. Th: Pa : U mass ratios 1200 : 1: 5.)

concentration is approximately 3 M in HCl. It is, therefore, to be expected that the "U curves" of Fig. 2 and Fig. 3 should differ considerably.

The separation experiment shown by the data of Fig. 2 was performed in glass equipment, using a 15-ml synthetic feed which was 5 M in HCl and which contained 5 mg of $Th^{230}$ ($1{\cdot}1 \times 10^8$ alpha counts per minute), 0·05 mg of $Pa^{231}$ ($2{\cdot}7 \times 10^6$ alpha counts per minute), $6 \times 10^6$ beta counts per minute of $Pa^{233}$, and 0·23 mg of $U^{233}$ ($2{\cdot}5 \times 10^6$ alpha counts per minute). Since, under the counting conditions employed, the beta counting-rate of the ionium sample was 0·9 beta counts per $10^3$ alpha counts, the analytical technique could not distinguish between 1% of the total Pa and zero Pa content of product 1. However, it is certain that the Pa products, i.e. products 5–9, contained greater than 98% of the tota Pa initially present in the feed. By alpha-pulse analysis[7] product 9 was shown to contain less than 0·1% of the total U.

Fig. 3 presents the data for a separation in equipment consisting of polyethylene contactors and holding tanks and Teflon stirrers, involving a feed prepared from an ionium-process waste. This "fluoride waste"[2] containing $HNO_3$, HF, rare earths, Th,

Pa, and U was contacted with TBP while solid $Al(NO_3)_3 \cdot 6H_2O$ was added in quantity sufficient to release the Pa from its fluoride complex.[2] The TBP extract, containing the Th, Pa, and U in respective 99+, approximately 90, and 94+% yields, with respect to the fluoride waste, was contacted with aqueous 3 M HF, the Pa reporting nearly quantitatively in the aqueous HF supernate, the U principally in the TBP phase, and the Th nearly quantitatively in the precipitate, which also contained rare earths. The aqueous HF supernate was precipitated with NaOH, the washed precipitate

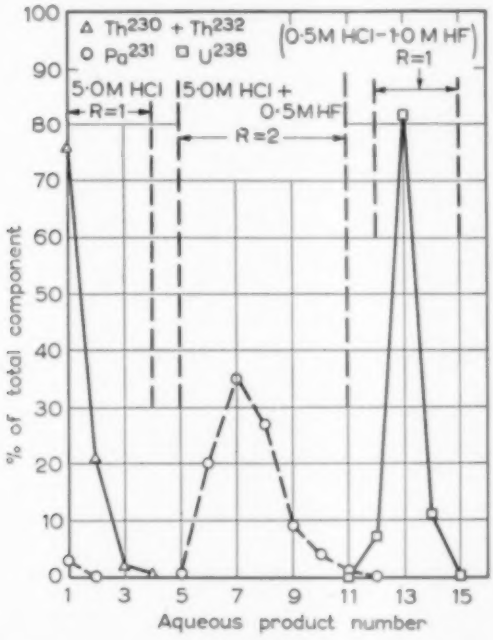


FIG. 3—Mutual separation of Th, Pa, and U from a feed prepared from an "ionium-process waste." (Four polyethylene contactors used. Th : Pa : U mass ratio 1 : 1 : 40.)

dissolved in HCl, the resulting solution precipitated with $NH_4OH$, the washed precipitate dissolved in HCl, the resulting solution evaporated to dryness, the resulting residue dissolved in 12 M HCl and the resulting solution (after being held at 80°C for 3 hours) diluted to form 200 ml of feed which was 5 M in HCl. This 200-ml portion of feed was contacted successively with four 200-ml portions of pre-equilibrated TBP. These TBP extracts were then scrubbed as shown in Fig. 3.

Analysis of these data showed the feed to contain 0·7 mg total Th, 0·7 mg $Pa^{231}$, and 28 mg total U. The yield of $Pa^{231}$ in the "Pa-products," i.e. aqueous products 5 to 11, was 97%, with a 35% yield in product number 7.

Since 3% of the Pa reported in product number 1, while none reported in products 2 to 4, it must be concluded that only 97% of the Pa was converted to extractable form in the feed preparation. It should be emphasized that in all separation experiments the final TBP phases were shown to be barren with respect to $Pa^{231}$. These facts, coupled with the data of Figs. 2 and 3, substantiate the conclusion, drawn from the data of Fig. 1 and Table 1, that "extractable" Pa behaves reversibly in the chemical

system considered. That is, of the Pa which is fed into the bank of contactors, that which is in "extractable" form will behave reversibly and appear in a well-defined Pa fraction, while that which is in "nonextractable" form will report quantitatively in the forepart of the Th fraction.

The protoactinium product phases (5 M HCl, 0·5 M HF) may be scrubbed with benzene to remove traces of TBP and stored in polyethylene containers. Such solutions are stable, the fluoride-complexed protoactinium showing no tendency to deposit on the container walls.

A sample stored in this manner for five years exhibited reversible behaviour. Within the limits of the determination, the total quantity of product in solution was the same as at the time of isolation of the sample, and the protoactinium was rendered TBP-extractable by addition of boric acid. (Boric acid releases the protoactinium from its fluoride complex through the formation of fluoroborate complexes. However, if an unnecessary excess of boric acid is present, the $K$ of Pa is lowered, presumably through complexing of TBP by boric acid or by one of its reaction products with HCl or HF.)

The method illustrated by the data of Fig. 3 has been used to isolate 15 mg of $Pa^{231}$ from the ionium-process "fluoride waste." It has also been applied to the isolation, in greater than 95% yield, of $Pa^{231}$ (and accompanying $Pa^{233}$) from neutron-irradiated ionium. In the latter separation, a second processing was necessary to eliminate the $Th^{228}$ which had grown from the $U^{232}$ parent during the Pa-U separation step.

## DISCUSSION

The rapid attainment of equilibrium in the HCl-TBP solvent extraction system is in strong contrast to the very slow rate of approach to equilibrium reported for the HCl—Dowex-1 anion exchange system.[4b] However, it is to be noted that the two methods of determining distribution coefficients differed in the important respect that in the HCl-TBP determinations "nonextractable" Pa was excluded, whereas in the ion-exchange studies of KRAUS and MOORE[4b] "nonadsorbable" Pa was not excluded.

These investigators have pointed out that in their Pa experiments involving HCl—Dowex-1 anion-exchange resin systems, "the distribution coefficients had not reached equilibrium values after one day of equilibration, particularly under conditions where $K$- is large." It is of interest to note that their graphically-presented data are consistent with the assumption of a feed containing a small percentage of Pa in "nonadsorbable" form corresponding to the "nonextractable" form noted in the present investigation, with the "nonadsorbable" form being slowly converted to the "adsorbable" form.

They do not report batch-distribution ratio determinations from the reverse direction, i.e. contacting a pregnant resin phase with an initially-barren aqueous HCl phase. However, they report column experiments in which the adsorbed Pa was not appreciably moved by 8 M HCl but was successfully eluted by aqueous phases which were less than 4 M in HCl. Consequently, it must be concluded that the behaviour of the adsorbed Pa is operationally reversible.

KRAUS, MOORE, and NELSON[11] have recently reported the mutual separation of Th, Pa, and U on a Dowex-1 column, using HCl and HCl + HF as eluting agents. The analogy between their ion-exchange separation and the presently-reported solvent-extraction separation is direct. In each of the techniques: the order of

[11] K. A. KRAUS, G. E. MOORE, and F. NELSON *J. Amer. Chem. Soc.* **78**, 2692 (1956).

appearance of products is Th(IV), Pa(V), and U(VI); the mutual separation of Pa(V) and U(VI) is difficult if the aqueous phase contains only HCl but readily accomplished if it contains both HCl and HF; and Pa of "nonadsorbable" and "nonextractable" form reports in the Th fraction.

In his study of $Pa^{233}$ in 0·1 to 3 M perchloric acid vs. the hydrogen form of Amberlite IRI2O cation-exchange resin, WELCH[12] reports a straight line of approximately unit slope in the double log plot of (Pa in the solution)/(Pa in the resin) vs. acidity of the solution indicating a protoactinium entity of unit positive charge. He postulates a $PaO_2^+$ ion in the perchloric-acid media investigated. ELSON[13] has postulated, partially on the basis of certain liquid-liquid partition data, that in 0·1 to 1·2 M perchloric-acid media the protoactinium entity carries a plus three charge and may be representable by $PaO^{+3}$ or $Pa(OH)_2^{+3}$, and that this entity is converted to one of higher positive charge, through stripping of oxygen or hydroxyl, at approximately 4·8 M $HClO_4$. He reaches the conclusion "that in high-acid solutions there is possibly the $Pa^{+5}$ solvated ion in solution."

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In line with these postulations, it may be noted, in Fig. 1, that although the curve for Pa(V) resembles that for U(VI) in the low-acid range, 0·5 to 4 M HCl, much more closely than that for Th(IV), in the intermediate-to high-acid range, 5 to 12 M HCl, it resembles the Th(IV) curve strongly and bears no resemblance to the U(VI) curve. (The dotted lines in Fig. 1 represent the U(VI) and Th(IV) smoothed curves following appropriate vertical shifts.) The displaced U(VI) curve is coincident with the Pa(V) curve in the 0.5 to 3 M HCl range. The displaced Th(IV) curve is nearly coincident with the Pa(V) curve in the 5 to 9 M HCl range. It is suggested that these facts are consistent with the assumption of an oxygenated protoactinium ion, roughly analogous to the uranyl ion in the low-acid range and a nonoxygenated protoactinium ion, roughly analogous to the thorium ion, in the high-acid range. Graphically (Fig. 1), 4·5 M HCl might be considered the critical concentration.

In interpreting the data of Fig. 1, the two highest Pa points should be considered suspect due to the difficulties involved in securing adequate phase disengagement to permit accurate measurement of $K$ values outside the range $10^{-4}$ to $10^4$. Outside this range, reproducibility does not necessarily imply accuracy. Inadequate phase disengagement results in a measured value too low for a $K$ greater than unity. Hence, it is possible that the far right-hand portion of the Pa curve is too low.

The nearly-identical operational HCl dependency in the 5 to 12 M HCl range for the extraction of Th(IV) and Pa(V) cationic entities assumed to bear positive charges of 4 and 5 respectively is unexpected and is probably to be explained as due to the profound changes in the properties of the two liquid phases with change in HCl concentration, rather than to identity of structure of extracting species. For example, in the 6 to 7 M HCl range the HCl dependency is operationally in excess of ninth-power for Pa(V) and for Th(IV).

The data of GOLDEN and MADDOCK[5c] for the extraction of Pa(V) from HCl into diisopropyl ketone show a similar high-power dependence on the HCl concentration. However, in contrast to the findings of these investigators, no difference was noted in the extraction behaviour of protoactinium when studied in "polyethylene" and in

[12] G. A. WELCH *Nature* **172**, 458 (1953).
[13] R. E. ELSON *The Actinide Elements* (McGraw-Hill Book Co., New York, N.Y., 1954), National Nuclear Energy Series, Plutonium Project Record, Vol. 14A, Div. IV, pp. 123–4.

glass equipment. In their "polythene" and glass equipment studies, involving $Pa^{231}$ and $Pa^{233}$ respectively, the $K$ values obtained in the former were nearly one hundred times as large as those obtained in the latter.

In the studies presently reported, both $Pa^{231}$ and $Pa^{233}$ data were obtained using equilibrium aqueous phases, which were 3·96 and 6·20 M in HCl, equilibrated TBP and diisopropyl ketone solvent phases, and both glass and polyethylene equipment, i.e. for each aqueous acid-solvent combination there were four permutations, each of which was run in duplicate. There were no statistically important differences in the data for the four permutations. The data for the HCl-TBP systems are included in Fig. 1. For the HCl–di-isopropyl ketone systems the $K$ values were 1·90 for 3·96 M HCl and 111 for 6·20 M HCl, agreeing very well with the "$Pa^{233}$-glass" data of GOLDEN and MADDOCK's Graph I.[5c]

It has been noted that traces of dibutyl phosphate (which may be formed by hydrolysis of TBP) greatly enhance the extraction of Pa(V). Since phosphate esters are widely used as plasticizers, it is possible that the "polythene" equipment used by GOLDEN and MADDOCK[5c] contained small quantities of di-isopropyl ketone-soluble phosphate esters capable of drastically changing the extractive properties of the solvent.

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 379 to 383. Pergamon Press Ltd., London

# THE SEPARATION OF CARRIER-FREE TELLURIUM TRACERS BY PAPER CHROMATOGRAPHY*

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(*Received* 18 *June* 1956)

**Abstract**—Paper chromatographic conditions for the purification of carrier-free tellurium tracers (from zirconium tracer and from copper in macro quantities), as well as for the separation of $Te^{IV}$ and $Te^{VI}$ ions, have been established. The low $R_F$ values of $Te^{VI}$ in butanol/HCl mixtures have been explained by the tendency of telluric acid to polymerization.

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THE method generally recommended[1,2] for the preparation of carrier-free tellurium tracer from fission products consists of the following operation: Preliminary purification in the presence of a copper salt used as a carrier; co-precipitation of the tellurium activity with iron hydroxide in the presence of dilute ammonia, which keeps the copper in solution, and final extraction of iron with isopropyl ether in 9-M HCl. The preparation thus obtained very often contains traces of iron which are difficult to eliminate by the solvent extraction method described above, and which if present even in very minute traces are not desirable for certain investigations. Secondly, it is difficult to obtain a good yield of tellurium activity by the extraction operation in the presence of strongly acidic solutions. Apart from these difficulties, the purification step based on co-precipitation of tellurium activity with iron hydroxide should be avoided as far as possible, since the latter can carry with it the activities due to other impurities[3] which might escape the preliminary purification step. These are, briefly, the considerations which led us to search for alternative methods for the purification of tellurium tracer obtained from fission products. In this article, applications of paper chromatography to the above problem, as well as to the problem of separation of $Te^{IV}$ and $Te^{VI}$, are described. It may be mentioned in this connection that an electrolytic method of purification of carrier-free tellurium tracer will be described elsewhere.[4]

For the purpose of this work, a source obtained from fission products, and containing a few hundred microcuries of $^{129}Te$, $^{127}Te$, and, initially, 10 millicuries of $^{132}Te$, was used. The latter isotope was eliminated by decay for about one month (i.e. ten times its half-life).

The radioactive characteristics of the product, however, indicated that it was significantly contaminated with some activity other than those of $^{129}Te$ and $^{127}Te$.

Efforts were therefore made to identify the carrier-free radioactive impurity.

The usual ascending techniques of one-dimensional paper chromatography were employed. Experiments were carried out with Whatman paper No. 1, at room

* This paper is part of a D. ès Sc. thesis of A. S. GHOSH MAZUMDAR.

[1] L. JACOBSON and R. OVERSTREET, Article no. 276, *Radiochemical Studies: The Fission Products* p. 1620 (1951).

[2] W. GARRISON and J. HAMILTON *Chem. Rev.* **49**, 239 (1951).

[3] L. GLENDENIN, Article no. 275, *Radiochemical Studies: The Fission Products* p. 1617 (1951).

[4] A. S. GHOSH MAZUMDAR and M. HAISSINSKY *J. Chim. Phys.*, in press.

temperature. Spots of macroscopic tellurium were revealed on the paper by a spray of an acidic solution of $SnCl_2$. In experiments involving carrier-free tracers, the usual counting techniques with a Geiger-Müller counter were adopted.

## IDENTIFICATION OF THE CONTAMINANT

A few millilitres of the contaminated source were evaporated with conc. hydrobromic acid on a water bath in order to reduce any $Te^{VI}$ to $Te^{IV}$, and then taken

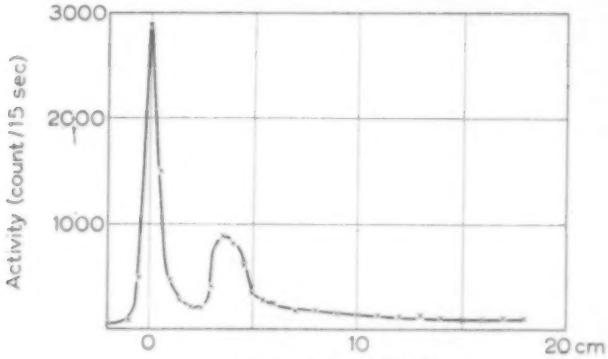


FIG. 1.—Butanol/HCl N.

up in a dilute acid. A few drops of this solution were used for examination by paper chromatography.

Two chromatograms, developed respectively with butanol saturated with HCl and a mixture of 30% methanol, 30% ethanol, and 40% 2 N HCl, were prepared and are illustrated in Figs. 1 and 2. Each showed only a peak corresponding to Te

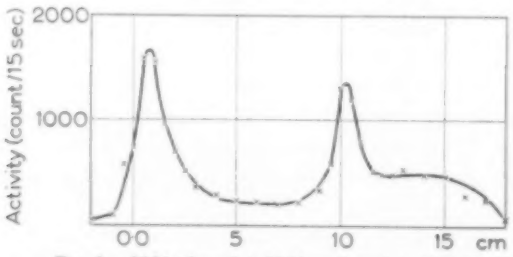


FIG. 2.—30% ethanol + 30% methanol + 40% 2N HCl.

and a peak at $R_F = 0$. It was deduced by comparison with published results on the separation of relevant species[5, 6] that the activity at $R_F = 0$ was most probably due to zirconium. An analysis of the radioactive characteristics of the species confirmed that it was in fact $^{95}Zr$.

## PREPARATION OF CARRIER-FREE TELLURIUM TRACERS FROM A MIXTURE CONTAINING MILLIGRAM QUANTITIES OF COPPER

In order to separate two ions by paper chromatography, it is desirable to find solvents in which the difference between the $R_F$ values of the two ions is of the order

[5] M. LEDERER *Anal. Chim. Acta* **5**, 185 (1951).
[6] H. GÖTTE and L. D. PÄTZE *Z. f. Electrochim.* **58**, 636 (1954).

of 0·1 or more. With a higher difference, the separation is obviously easier and cleaner. Of the following solvents previously examined by other workers, the second, third, and fourth are therefore suitable for the separation of $Te^{IV}$ from $Cu^{II}$:

| Solvents | $R_F$ values | |
|---|---|---|
| | $Cu^{II}$ | $Te^{IV}$ |
| (1) Butanol/HCl N | 0·10[5] | 0·18[5] |
| (2) Butanol/HCl 2N | 0·13 | |
| | 0·11[7] | 0·47[8] |
| (3) Butanol/HCl 3N | 0·20[7] | 0·67[8] |
| (4) Butanol/HBr 10% | 0·15[5, 8] | 0·46[5, 8] |
| (5) Butanol/HBr 20% | — | 0·92[5, 8] |

The above figures indicate also clearly that the difference between the $R_F$ values of these ions tends to increase as the acidity of the solvent increases. From the above trend, it was thought that the difference would probably be still greater with

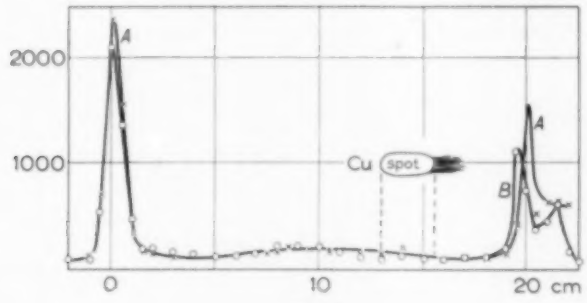


FIG. 3.

solvent No. 5, which was therefore tried. The $R_F$ values experimentally determined with macroscopic spots justify this expectation. The values reported below were not significantly affected when the ions were present as a mixture. We have further confirmed that with this solvent the peak due to carrier-free tellurium tracer was well ahead of the macro spot of $Cu^{II}$ on a chromatogram. $R_F$ values for $Cu^{II}$, $Te^{IV}$, and $Te^{VI}$ are respectively 0·20, 0·93, and 0·11. The spots of $Te^{IV}$ and $Te^{VI}$ are connected by a comet.

Finally, we tried another solvent: 90% acetone + 5% water + 5% conc. hydrochloric acid, with which BURSTALL and others[7] have reported for $Cu^{II}$ an $R_F$ value of 0·61–0·80. The values experimentally found by us with macroscopic quantities of $Te^{IV}$, $Te^{VI}$, and $Cu^{II}$ are as follows: 0·96, 0·07, and 0·69 (the copper spot tends to diffuse ahead of the main spot). These values are not significantly different when the ions are present as a mixture.

Fig. 3 represents two chromatograms obtained with this solvent. Curve *A* corresponds to a mixture of macroscopic copper with our contaminated source

[7] F. H. BURSTALL, G. R. DAVIES, R. P. LINSTEAD, and R. A. WELLS *J. Chem. Soc.* 516 (1950).
[8] M. LEDERER *Microchim. Acta.* 43 (1956).

containing tellurium tracer, while curve *B* corresponds to the copper-free source. The position of the macro spot of copper is indicated. Each of these two chromatograms contains two peaks: one, corresponding to $R_F = 0$, is evidently due to $^{95}Zr$ present as impurity; the other one, corresponding to radio-tellurium, is, however, sufficiently ahead of the macro spot of copper. Hence, this solvent is also quite suitable for the separation under investigation.

In the preceding experiments, the amount of copper involved was just sufficient to produce a macro spot on the filter paper, and was thus much below milligram quantities. The following experiment was therefore undertaken to see how the chromatographic separation of tellurium tracer would take place when the quantity of copper present in the mixture was of the order of a few milligrams:

7 mg of copper chloride were mixed with a major fraction of the source referred to above. The mixture was twice evaporated on a water bath with concentrated hydrobromic acid in order to reduce the whole of the tellurium to the valency state of IV. The residue was taken up with a very small volume of dilute hydrobromic acid. Half of this active solution was then applied as a narrow strip along the breadth (25 cm) of a filter paper, on which a chromatogram was developed with butanol saturated with 20% HBr. It was confirmed that the separation of tellurium tracer was feasible even in presence of milligram quantities of copper salts. There was, nevertheless, some chance of contamination in view of the tendency of the band due to $Cu^{II}$ to diffuse ahead of the main band. It is therefore considered advisable either to repeat the operation or to undertake the separation in several batches, so that the quantity of copper salts for each chromatogram of 25-cm breadth does not exceed 2 mg. For final extraction of pure tellurium tracer, the corresponding portion of the chromatogram was cut apart and treated with hydrochloric acid (1 : 1). The tracer preparation, though quite pure radiochemically, contained some acid soluble matter which had come from the filter paper.

## SEPARATION OF $Te^{IV}$, $Te^{VI}$

Table 1 contains the $R_F$ values as found by experiment of $Te^{IV}$ and $Te^{VI}$ ions in different solvents. It also contains certain values reported by one of us. It will be seen that each of the solvents Nos. 1, 2, 3, and 5 gives rise to a sufficiently wide difference in the $R_F$ values of $Te^{VI}$ and that of $Te^{IV}$, so as to lend itself to the desired separation. For this purpose, solvents Nos. 3 and 5 seem to be the best, whereas 4 and 6 are totally useless.

### *Discussion*

The existence of a long comet in the case of solvent No. 4 may be explained in terms of a gradual reduction of $Te^{VI}$, induced by concentrated hydrobromic acid.

Besides the practical value in regard to separation, these results have the following theoretical interest. It is known that the $R_F$ values of anions are generally high in butanol/HCl mixture. For instance, the $R_F$ values of orthophosphate, arsenate, arsenite, selenite, sulphate, perrhenate, and pertechnetate are respectively 0·7–0·8, 0·9–1·0, 0·7, 0·7, 0·6, 1·0, and 1·0, with butanol/normal HCl.[9, 10] On the other hand, the $R_F$ values of polyacids are very low; for example, the $R_F$ for polyphosphate is

[9] M. LEDERER *Anal. Chim. Acta* **11**, 524 (1954).
[10] M. LEDERER *Anal. Chim. Acta* **12**, 146 (1955).

TABLE 1.—$R_F$ VALUES OF $Te^{IV}$ AND OF $Te^{VI}$

| Solvents | $R_F$ values | |
|---|---|---|
| | $Te^{IV}$ | $Te^{VI}$ |
| (1) Butanol/HCl N | 0·18[8] | |
| | 0·17 | 0·04 |
| (2) Butanol/HCl 2N | 0·47[8] | |
| | 0·45 | 0·08 |
| (3) Butanol/HCl 3N | 0·67[8] | |
| | 0·77 | 0·16 |
| (4) Butanol/HBr 20% | 0·92[8] | |
| | 0·93 | 0·11, with a comet extending up to the spot having $R_F = 0·93$ |
| (5) 90% acetone + 5% water + 5% conc. hydrochloric acid | 0·95 | 0·07 |
| (6) 30% methanol + 30% methanol + 40% HCl 2N | 0·56 | 0·57, with a tail. |

0·0–0·2 in the same solvent.[9] This has been explained by the assumption that the phenomenon of polymerization is predominant in the latter case. In so far as $Te^{IV}$ and $Te^{VI}$ ions are concerned, the former is known to behave as a cation in acidic mediums,[8, 11] whereas for the latter, the $R_F$ remains very low even if the concentration of acid in the solvent increases. By analogy, it may therefore be concluded that, under the conditions of our experiments, telluric acid exists in a polymerized form. This conclusion is in agreement with the observation of ANTIKAINEN,[12] according to whom telluric acid forms autocomplexes even in dilute solutions.

[11] R. SCHUMANN *J. Amer. Chem. Soc.* **47**, 356 (1925).
[12] P. J. ANTIKAINEN *Suomen Kemistilheti* **28**, 135 (1955).

J. Inorg. Nucl. Chem., 1957, Vol. 3, pp. 384 to 387. Pergamon Press Ltd., London

# SEPARATION OF THORIUM AND URANIUM NITRATES BY ANION EXCHANGE

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(*Received* 12 *October* 1956)

**Abstract**—The anionic character of thorium in nitric acid solutions has been investigated and distribution coefficients measured. The results have been employed to effect a separation of thorium and uranium by anion exchange.

## INTRODUCTION

A GREAT deal of work on ion exchange of chloride solutions, particularly in relation to cation exchange, has been reported. However, information regarding the anion-exchange behaviour of nitrate solutions is scant.

The existence of anionic nitrate complexes of thorium and cerium is recorded by YOST,[1] although HYDE[2] reports that thorium forms no such complexes in nitric-acid solutions of any concentration and can be separated by anion exchange from metals which do form negative ions. The reluctance of thorium to form anionic complexes also gains support from a detailed study of the chloride system reported by KRAUS.[3] According to another recent reference,[4] thorium shows anionic character in nitric-acid solution, and mixtures of thorium and cerium in 6 M nitric acid have been separated on an anion exchanger. The thorium is retained on the column, while the cerium passes through. Unpublished information by ATKINS, PHILLIPS, and JENKINS in these laboratories with natural uranium in 7 M nitric acid has also indicated that thorium (as $UX_1$) is retained on De-Acidite FF.

The anionic character of thorium nitrate solutions has a bearing on aqueous processing in the thorium–uranium-233 reactor cycle, and an attempt has therefore been made to settle the conflicting evidence. This paper describes experiments which show that thorium does exhibit anionic properties in nitric-acid solutions and is in fact more anionic in character than corresponding uranium solutions. Volume distribution coefficients

$$D_v = \frac{\text{Activity in resin}}{\text{Volume of resin}} \times \frac{\text{Volume of solution}}{\text{Activity in solution}}$$

for thorium and uranium are shown in Fig. 1. This figure also includes values of $D_v$ for thorium, as $UX_1$, and for uranium with a different batch of De-Acidite FF (60–100 mesh) obtained by ATKINS, PHILLIPS, and JENKINS. They have

* Australian Atomic Energy Commission Attached Staff.

[1] D. M. YOST, H. RUSSELL JR., and C. S. GARNER *The Rare-earth Elements and Their Compounds* John Wiley and Sons Inc., N.Y. p. 61 (1947).

[2] E. K. HYDE Int. Conf. on the Peaceful Uses of Atomic Energy P/728 (1955).

[3] K. A. KRAUS, G. E. MOORE, and F. NELSON *J. Amer. Chem. Soc.* **78**, 2692 (1956).

[4] YING-MAO CHEN, CHIA-TSUNG LIN, and TUNG-HO CHEN *J. Chinese Chem. Soc.* (Taiwan) *Ser.* **11**, **2**, 111 (1955). cf. *Chem. Abs.* **49**, 15619 g (1956).

confirmed by chemical analysis for thorium that the systematic discrepancies revealed in Fig. 1 are attributable to the different batches of resin. The anionic property of thorium is further illustrated by the quantitative separation of thorium and uranium carried out with a De-Acidite FF column.

## EXPERIMENTAL

### *Distribution coefficient measurements*

De-Acidite FF (settling rate 3–1·4 cm/min) was cycled through the $OH^-$ form into the $NO_3^-$ form and stored under very dilute nitric acid. Before use, the resin was twice equilibrated with nitric acid of the normality to be used. In each case the volume of resin used was of the order of 1 ml, and equilibrium was established by stirring overnight (16 hr) at room temperature. The thorium determination was carried out using $Th^{230}$ tracer and the uranium determination using $U^{233}$. Decomposition of the resin at and above 6 M nitric acid was noted and caused somewhat inconsistent results in the high-acid region (cf. KRAUS[5]).

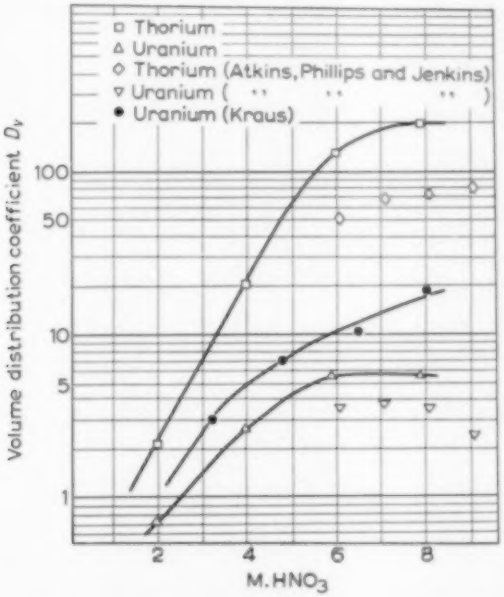


FIG. 1.—Volume distribution coefficients for thorium and uranium.

### *Separation of thorium and uranium*

Separation at room temperature was not good, so an apparatus similar to that described by THOMPSON[6] was used at 77°C. The bed was approximately 2 mm diameter × 8 cm long. The resin (De-Acidite FF, settling rate 1·4–0·6 cm/min) was cycled through the $OH^-$ to the $NO_3^-$ form and was finally conditioned with 6 M nitric acid which had been previously briefly boiled. The active solution containing $Th^{230}$ and $U^{233}$ in one drop of 6 M nitric acid was placed on the column, then one drop of 6 M nitric acid was passed through. Elution was commenced at 1 drop per 2 min with 4 M nitric acid which had been briefly boiled immediately before use and the actual concentration of which was therefore slightly greater than 4 M. After the uranium had been eluted, the eluant was changed to water in order to remove the thorium.

[5] K. A. KRAUS and F. NELSON Int. Conf. on the Peaceful Uses of Atomic Energy P/837 (1955).
[6] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN, and G. T. SEABORG *J. Amer. Chem. Soc.* **76**, 6229 (1954).

Three peaks in all were observed (Fig. 2): a sample from each, as well as one from the tail of the uranium curve, was examined by alpha-pulse analysis. The first peak contained daughters (mainly radium) from the $Th^{230}$ and $U^{233}$ decay series. In the uranium peak no thorium was detected and in the thorium peak no uranium could be detected. No thorium was found in a sample taken from the point where the eluant was changed from 4 M nitric acid to water. After the addition of the water, there was some mechanical breakdown of the resin which resulted in a reduced flow rate and a particularly steep leading edge to the thorium elution peak. More pressure was applied to the column. This resulted in a rapid flow rate with a sharp drop and a long tail on the trailing edge.

## DISCUSSION

The anionic character of thorium in nitric acid has been established in this paper and used as a means of separating it from uranium. The method is suited to laboratory scale separation of nitrate solutions.

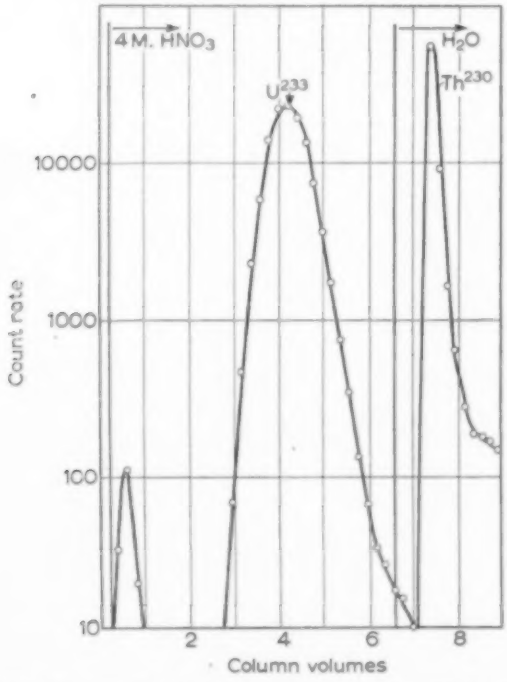


FIG. 2.—Elution of uranium and thorium from De-Acidite FF (settling rate 1·4–0·6 cm/min with 4 M $HNO_3$ and $H_2O$ at 77°C from a column 2 mm × 8 cm at a flow rate of 1 drop per 2 min.

Distribution coefficient measurements for uranyl nitrate are somewhat lower than those given by KRAUS,[5] which apply to a different resin. The position of the uranium maximum at four geometric column volumes gives $D_e = 3{\cdot}5$ from the relation $D_e = 1/E - i$ (ref. 5).

The elution curve shows quantitative separation of the elements under the conditions which have been described. Separation of the elements was not obtained in a column operated at room temperature. This may have been due to a delay in reaching equilibrium.

The complex-formation constants for thorium in the chloride system decrease rapidly as the number of ligands increases.[7] Thorium would thus not be expected to form anionic chloride complexes, and their absence has been confirmed by KRAUS.[3]

A similarity in nitrate complexing of thorium and plutonium(IV) exists, and there is evidence for both elements for complexes such as $M(NO_3)_6^{--}$ in high concentrations of nitric acid.[8]

*Acknowledgements*—The assistance and suggestions of Dr. C. J. HARDY are gratefully acknowledged. The author is also indebted to Dr. J. M. FLETCHER and Mr. H. A. C. M$^{c}$KAY for helpful discussion, and to Mr. D. H. ATKINS, Mr. G. PHILLIPS, and Mr. E. N. JENKINS for permission to include in Fig. 1 results by them.

[7] L. I. KATZIN Chap. 4, p. 70 *The Actinide Elements* Nat. Nucl. Energy Series, Div. IV, Vol. 14A McGraw-Hill, N.Y. (1954).
[8] J. C. HINDMAN Chap. 9, p. 341, *ibid.*

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# LETTER TO THE EDITORS

## Discharge-induced formation of boron polymers

(*Received* 22 *October* 1956)

We have recently observed that a mixture of a trichloroborane and carbon monoxide, when subjected to the action of an ozonizer-type discharge, produces an apparently polymeric solid possessing properties not commonly associated with boron compounds.

The one-metre-long discharge apparatus consisted of two coaxially sealed Pyrex glass tubes. The inner tube was 10 mm in diameter and was filled with mercury; the outer tube was 32 mm in diameter and was wrapped with aluminium foil. The mercury well and aluminium foil were then connected to a 12,000-volt luminous-tube transformer. A 1-litre bulb was attached to one end of the discharge tube to provide additional volume, and the assembly was connected to the vacuum system through a mercury float-valve. In a typical experiment, a mixture which furnished an 18·65-mm pressure of trichloroborane (1·880 millimoles) and a 58·08-mm pressure of carbon monoxide (5·821 millimoles) was subjected to the action of an 11,000-volt discharge.

A gradual diminution in total pressure occurred, and at the end of 160 hours the discharge-tube walls were observed to be coated with a transparent, light yellow film. Separation of the volatile contents showed that all of the trichloroborane had disappeared and that only 39·5% (2·301 millimoles) of the carbon monoxide charged was still present. Since only a negligible amount of volatile matter other than carbon monoxide was recovered, and since the nonvolatile product seemed to be homogeneous, it seems reasonable to assign to the latter the empirical formula $BCl_3{\cdot}2CO$.*

A separate experiment identical with that described above, except that all contact of the reactants with mercury during the discharge process was prevented, also yielded the polymeric product.

The nonvolatile product, which could be stripped away from the walls as a film, had a cedar-like odour. Its softening point was approximately 115°C. A sample of about 5 mg, when added to 1 ml of water, conferred upon the latter the consistency of raw egg-white. This consistency was reproduced when the mixture was boiled to dryness and fresh water was added. Addition of silver nitrate to the water "solution" produced no silver chloride.

The film-like product was insoluble, or only sparingly soluble, in carbon tetrachloride and diethylether. In ethanol, it dissolved readily without apparent effect on the mobility of the solvent to yield a yellow solution. On prolonged exposure to air, it lost its transparency and became white. Addition of the white solid to water produced the same effect as that previously described for the transparent film.

Preliminary experiments indicate that silicon tetrachloride and carbon monoxide can undergo a similar reaction to produce a nonvolatile, viscous liquid. Extraction of the latter with diethyl ether yields needle-shaped, colourless crystals. A preliminary experiment using trifluoroborane and carbon monoxide produced a film somewhat similar in appearance to that obtained with trichloroborane. Further studies on this product are in progress.

The authors gratefully acknowledge the support given to this work by the Air Force Office of Scientific Research.

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*College of Chemistry and Physics,*
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* Tentative confirmation of this empirical formula has been obtained through preliminary chemical analysis.

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The one-metre-long discharge apparatus consisted of two coaxially sealed Pyrex glass tubes. The inner tube was 10 mm in diameter and was filled with mercury; the outer tube was 32 mm in diameter and was wrapped with aluminium foil. The mercury well and aluminium foil were then connected to a 12,000-volt luminous-tube transformer. A 1-litre bulb was attached to one end of the discharge tube to provide additional volume, and the assembly was connected to the vacuum system through a mercury float-valve. In a typical experiment, a mixture which furnished an 18·65-mm pressure of trichloroborane (1·880 millimoles) and a 58·08-mm pressure of carbon monoxide (5·821 millimoles) was subjected to the action of an 11,000-volt discharge.

A gradual diminution in total pressure occurred, and at the end of 160 hours the discharge-tube walls were observed to be coated with a transparent, light yellow film. Separation of the volatile contents showed that all of the trichloroborane had disappeared and that only 39·5% (2·301 millimoles) of the carbon monoxide charged was still present. Since only a negligible amount of volatile matter other than carbon monoxide was recovered, and since the nonvolatile product seemed to be homogeneous, it seems reasonable to assign to the latter the empirical formula $BCl_3{\cdot}2CO$.*

A separate experiment identical with that described above, except that all contact of the reactants with mercury during the discharge process was prevented, also yielded the polymeric product.

The nonvolatile product, which could be stripped away from the walls as a film, had a cedar-like odour. Its softening point was approximately 115°C. A sample of about 5 mg, when added to 1 ml of water, conferred upon the latter the consistency of raw egg-white.This consistency was reproduced when the mixture was boiled to dryness and fresh water was added. Addition of silver nitrate to the water "solution" produced no silver chloride.

The film-like product was insoluble, or only sparingly soluble, in carbon tetrachloride and diethylether. In ethanol, it dissolved readily without apparent effect on the mobility of the solvent to yield a yellow solution. On prolonged exposure to air, it lost its transparency and became white. Addition of the white solid to water produced the same effect as that previously described for the transparent film.

Preliminary experiments indicate that silicon tetrachloride and carbon monoxide can undergo a similar reaction to produce a nonvolatile, viscous liquid. Extraction of the latter with diethyl ether yields needle-shaped, colourless crystals. A preliminary experiment using trifluoroborane and carbon monoxide produced a film somewhat similar in appearance to that obtained with trichloroborane. Further studies on this product are in progress.

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* Tentative confirmation of this empirical formula has been obtained through preliminary chemical analysis.

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